THE NICKEL BULLETIN

A Monthly Summary of Recent Literature

APRIL

1960 Volume 33 No. 4

THE MOND NICKEL COMPANY LIMITED
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ABSTRACTS OF CURRENT PUBLISHED INFORMATION ON NICKEL AND ITS ALLOYS

NICKEL

Refining of Nickel/Copper/Cobalt Mattes

R. F. PEARCE, J. P. WARNER and V. N. MACKIW: 'A New Method of Matte Refining by Pressure Leaching and Hydrogen Reduction.'

Jnl. Metals, 1960, vol. 12, Jan., pp. 28–32.

Development work on the refining of nickel, carried out by Sherritt Gordon Mines, Ltd., has extended the use of pressure leaching to treatment of enriched products, in particular, mattes. This account of the hydrometallurgical processes involved, and of the application of these processes to the treatment of mixed mattes, is based on the paper presented by the authors at the 1959 Meeting of the American Institute of Mining, Metallurgical and Petroleum Engineers: see abstract in *Nickel Bulletin*, 1959, vol. 32, No. 8, pp. 244–5.

Surface Energy of Solid Nickel

E. R. HAYWARD and A. P. GREENOUGH: 'The Surface Energy of Solid Nickel.'

Jnl. Inst. Metals, 1960, vol. 88, Jan., pp. 217–20.

At temperatures near the melting point, thin sheets or small-diameter wires of many metals deform under the stresses produced by surface-energy effects. It is possible to determine the load that will just balance these effects and inhibit deformation, and, hence, to measure the surface energy of the metal. In the experiments reported, the surface energy of pure nickel wire in argon was measured by the method employed, on copper wire, by UDIN, SHALER and WULFF (*Trans. Amer. Inst. Mining and Metallurgical Engineers*, 1949, vol. 185, p. 186).

At 1250°C. and at the melting point, the surface energy of nickel was found to be 1850 ergs. cm.$^{-2}$ and 1725 ergs.cm.$^{-2}$, respectively: these results are in agreement with theoretical estimates. Experimental evidence indicates that the wires deform by the Nabarro–Herring diffusion mechanism.

The activation energy for self-diffusion determined in the present work (49·5 kcal/g-atom) is considerably less than the value of 66·5 kcal/g-atom obtained using radioactive-tracer techniques.

Effect of Plastic Deformation on the Diffusion of Hydrogen in Nickel

H. H. GRIMES: 'The Effect of Plastic Deformation on the Diffusion of Hydrogen in Nickel.'

Acta Metallurgica, 1959, vol. 7, Dec., pp. 782–6.

The experiments described were designed to study interstitial diffusion in a system subjected to both elastic and plastic strains (up to ten per cent. total strain) at temperatures in the range 430°–850°C., and, specifically, to determine the rate of permeation of hydrogen through tubular specimens of nickel stressed elastically in tension at constant load, or plastically at constant strain rate. The system hydrogen in nickel was selected for study on four accounts: the diffusion process is known to be rate-determining for the temperatures and pressure employed; the system is free from compound formation; phase changes are absent in the experimental range studied; and the high rate of diffusion permits accurate experimental measurements.

No significant change in the diffusion coefficient was observed for deformations of up to 10 per cent., a finding which is in agreement with a theoretical analysis of interstitial diffusion in strained systems, based upon considerations of interatomic forces and strain gradients.

The diffusion coefficient for hydrogen through unstrained nickel in the temperature range studied can be represented by the equation:

$$D = 0{\cdot}0095 \exp(-10{,}300/RT) \text{ cm.}^2/\text{sec.}$$

Corrosion-Resistance of Nickel

See abstract on p. 89.

Influence of Nickel Additions on the Oxidation Behaviour of Copper

See abstract on p. 79.

Study of Nickel-containing Glasses

B. K. BANERJEE: 'Studies on Cobalt-containing and Nickel-containing Glasses.'

Jnl. Soc. Glass Technology, 1959, vol. 43, pp. 405t–16t.

The studies described were carried out, using magneto-chemical and X-ray techniques, on cobalt-containing and nickel-containing coloured glasses, with the aim of establishing the rôle of the colouring constituent in the glass structure. In general, the glasses were of alkali/boric-oxide base, varying in the amounts of alkali; a few glasses of silicate and ternary-borate type were also investigated.

The following aspects of the problem are discussed: (1) the influence of glass composition on the state of the colouring oxide; (2) the relationship between the concentration of the colouring oxide and its state in the glassy matrix; (3) the influence, on the state of the colouring oxide in the glass structure, of time and temperature of heating, and (4) the

possible rôle of the colouring constituent in the glass structure.

The various theories advanced in explanation of the origin of colour in glass are discussed. The observations made during the present investigation are interpreted in terms of colour produced by solution of the metallic ion, and it is deduced, from measurements of magnetic properties at low temperatures, that the binding in the tetrahedral and octahedral complexes is ionic.

Titrimetric Determination of Nickel in Non-Ferrous Alloys

V. A. NELSON and L. J. WRANGELL: 'Application of EDTA to Titrimetric Determination of Nickel in Non-ferrous Alloys.'

Analytical Chemistry, 1960, vol. 32, Jan., pp. 99–103.

The titrimetric and gravimetric procedures previously employed by the authors' Company to determine nickel in non-ferrous alloys entailed the use (prior to dimethylglyoxime precipitation of nickel) of hydrogen sulphide to remove copper, which would otherwise interfere. The titrimetric method has the further disadvantage that the titrant (standard cyanide solution) requires frequent restandardization. It is reported in the literature that nickel has been successfully titrated with disodium dihydrogen (ethylenedinitrilo)-tetraacetate (EDTA), and that EDTA has been used also in the titrimetric determination of nickel in steel after separation of nickel from other metal ions. In applying EDTA to the determination of nickel in non-ferrous alloys, it was assumed that it would be necessary to separate nickel from copper, and perhaps from other metal ions. It was therefore proposed to use dimethylgyoxime for the precipitation of nickel, without previous hydrogen-sulphide separation of copper. It was not, however, known whether a single precipitation would adequately separate the nickel from copper and other metal ions prior to titration with EDTA. In the present paper the authors record the results of the investigation which they carried out to determine ways of separating the nickel, the indicators suitable for titration, and the effects of diverse ions on the titration.

Details are given of two variants of the procedure finally evolved: one for use in the presence, the other in the absence, of interfering iron and cobalt. Separation and purification of nickel are accomplished by double precipitation of dimethylglyoxime, and interferences caused by cobalt, iron and tin are avoided. 'Cal Ver 1' is selected as the indicator.

The technique has been applied to a wide range of non-ferrous-alloy standards containing from 0·16 to 66·38 per cent. nickel. Based on the 95 per cent. confidence level, limits of error for nickel contents in the ranges 0·16–0·6 and 30·8–66·38 per cent. are ±0·03 and ±0·21 per cent., respectively.

Determination of Nickel and Cobalt in Alloys and Stainless Steels

L. L. LEWIS and W. A. STRAUB: 'Determination of Nickel and Cobalt in High-Alloy and Stainless Steels.'

Analytical Chemistry, 1960, vol. 32, Jan., pp. 96–9.

The investigation described was initiated to satisfy the need which, with the increase in the complexity and production of alloys and stainless steels, has arisen for a more rapid and reliable method of determining large amounts of nickel and cobalt in such materials.

In recent years both nickel and cobalt have been titrated successfully with EDTA, but to enable application of this technique to analysis of high-alloy steels, some means had to be found of separating the two elements from each other, and from other alloying elements, prior to titration. In the process finally evolved the nickel is isolated from other elements by dimethylgloxime precipitation (with or without a preliminary ion-exchange separation) and cobalt is isolated by ion exchange. The separated metals are then determined by titration with EDTA. Full details are given of the reagents and procedures employed.

Typical results, presented for seven steels and cobalt-nickel alloys covering the relevant range of composition, show a standard deviation, for a single determination, of 0·05 per cent. for nickel and 0·08 per cent. for cobalt. The method, which is claimed to combine the advantage of speed with the accuracy of commonly used techniques, is applicable to a wide variety of high-alloy and stainless steels.

ELECTRODEPOSITION AND OTHER COATING METHODS

Chemistry of Electroless Nickel Plating

G. GUTZEIT: 'An Outline of the Chemistry Involved in the Process of Catalytic Nickel Deposition from Aqueous Solution. Parts I–IV.'

Plating, 1959, vol. 46, Oct., pp. 1158–64; Nov., pp. 1275–8; Dec., pp. 1377–8; 1960, vol. 47, Jan. pp. 63–70.

Selective deposition, by catalytic reduction from aqueous solutions, of an adherent amorphous nickel-phosphorus coating on metallic substrates (so-called 'electroless' plating) was first described by BRENNER and RIDDELL in 1946–47. Electroless plating is based on the controlled autocatalytic reduction of nickel cations, by means of hypophosphite anions, in the presence of water. (While both alkaline and acid plating solutions have been used, most commercial baths to-day operate at a pH of less than 6·0.) In the years 1947–52 work by the General American Transportation Corporation culminated in the development of a commercial process which is now available under the tradename 'Kanigen'. Since its advent, the 'Kanigen' process has gained acceptance in a wide range of industries, in which advantage has been taken

of its capacity, *inter alia*, to deposit, on both non-metallic and metallic materials, nickel coatings which are of uniform thickness, of a hardness which can be further increased by heat-treatment, of satisfactory corrosion-resistance, and relatively free from porosity.

This paper comprises a detailed review of (1) the fundamental chemical reactions involved in electroless plating, and (2) the influence of solution composition and operating conditions on the performance of baths for continuous plating*.

The review is based on a *bibliography* of 33 items of literature. The information in the text is supplemented by numerous tabular and graphical data.

Microthrowing Power of Nickel-Plating Solutions

L. B. GARMON and H. LEIDHEISER: 'Experimental Studies of the Electrodeposition of Metal in Narrow Crevices.'

46th Ann. Tech. Proc., Amer. Electroplaters' Soc., 1959, pp. 50–60; disc., p. 360.

Report issued under the aegis of *A.E.S. Research Project No.* 17.

The research covered by Project No. 17 was initiated with the aim of obtaining a better understanding of the factors governing the distribution of an electrodeposit on a micro-scale. Since many of the experiments necessary for the achievement of this aim are not yet completed, it is emphasized that this paper, the first relating to the experimental phase of the project, is essentially a progress report.

The work described was concerned with the distribution of coatings deposited (from nickel, copper and cobalt plating solutions) within a crevice 0·07–2·1 mm. wide and 8 mm. deep. A study was made of the influence, on the total amount of deposit formed within the crevice and on the variation in thickness as a function of depth within the crevice, of the following variables: crevice width, solution composition, metal-ion concentration, temperature, current density, stirring, and solution purification. Full details are given of the apparatus and procedures employed.

In general, the amount of metal deposited in the crevice increased with increase in the metal-ion concentration and in the conductivity of the solution. The nickel solutions studied are placed, according to their capacity to produce a large amount of deposit in the crevice, in the following descending order of effectiveness: all-chloride solution, Watts solution, all-sulphamate solution, and all-sulphate solution.

Electrodeposition of Nickel Alloys from Pyrophosphate Solutions

T. L. R. CHAR: 'Electrodeposition of Nickel Alloys from the Pyrophosphate Bath.'

46th Ann. Tech. Proc., Amer. Electroplaters' Soc., 1959, pp. 76–80; disc., pp. 363–4.

Experiments carried out in the author's laboratory have demonstrated that nickel can be co-deposited with tin, copper, zinc, cobalt or iron from pyrophosphate plating solutions. In this paper he summarizes the optimum plating conditions established for each alloy, and discusses the findings of a study of (*a*) the influence of the plating variables on deposit composition, cathode efficiency and potential; (*b*) the conditions governing satisfactory deposition of alloys over a wide range of composition; and (*c*) the structure of the deposits and anode behaviour.

The constituents of the respective plating solutions are noted below:

Tin–Nickel Solution: nickel chloride, stannous pyrophosphate, potassium pyrophosphate, ammonium citrate.

Nickel–Copper Solution: nickel chloride, copper pyro-phosphate, potassium pyrophosphate.

Nickel–Zinc Solution: nickel chloride, zinc pyrophosphate, potassium pyrophosphate.

Nickel–Cobalt Solution: nickel chloride, cobalt chloride, potassium pyrophosphate, ammonium citrate.

Nickel–Iron Solution: nickel chloride, ferric chloride, potassium pyrophosphate.

Preliminary investigations of the feasibility of depositing nickel-manganese, nickel-tungsten, and nickel-molybdenum alloys have produced promising results. Solution compositions and operating conditions are tabulated.

Deposition and Properties of 'Micrograin' Nickel

H. D. HUGHES: 'Grain-Size Control in Electroforming.'

46th Ann. Tech. Proc., Amer. Electroplaters' Soc., 1959, pp. 326–32; disc., p. 388.

De-icer elements of the type fitted to the leading edge of most propeller blades are subjected not only to erosion caused during flight through rain or cloud but also to impact damage from stones and dust thrown up during landing. The work described by the author was concerned with the development of a procedure capable of producing an electroform which would (1) conform closely to the configuration of, and which could thus be readily attached to, the element, and (2) exhibit the impact strength, fatigue strength, lightness, and resistance to corrosion and erosion necessary for use as a protective sheath.

The process ultimately evolved takes advantage of the tendency of electrodeposited nickel to reproduce the grain-size of the basis metal. A thin flexible sheet of very finely milled graphite particles, bonded together with a resin binder, is attached to a mandrel and is copper flashed. The flash coating, adopting the surface structure of the graphite sheet, has a grain-size far smaller than is obtainable by normal methods. Nickel is then electrodeposited (from a Watts solution) to the

* In this connexion, see also paper by DE MINJER and BRENNER reporting the findings of a study of the fundamental variables affecting deposition from such solutions: abstract in Nickel Bulletin, 1958, vol. 31, No. 3, pp. 71-3.

requisite thickness, the composite sheet is removed from the mandrel, and separation from the graphite layer is effected by means of organic solvents. The nickel electroform which remains is then ready for bonding into position as a protective sheath. Such 'Micrograin' nickel can be produced to hardnesses higher than 500 V.P.N., and, in contrast to most nickel coatings, exhibits compressive stress. The deposits are also extremely flexible.

The present paper gives full details of the stages involved in the production of 'Micrograin' nickel, presents data illustrating the hardness, tensile strength and ductility obtainable, and discusses the structure and stress associated with such deposits. Notes are included on tests carried out on 'Micrograin' sheaths fitted to propeller blades.

Adhesion of Electrodeposited Nickel to Chromium at Elevated Temperatures

W. E. REID and F. OGBURN: 'The Adhesion of Electrodeposited Nickel to Chromium at Elevated Temperatures.'

Jnl. Electrochemical Soc., 1960, vol. 107, Feb., pp. 91-3.

The use of a nickel+chromium composite electrodeposited coating as a means of protecting molybdenum from oxidation at elevated temperatures has been described by COUCH *et al.* (see abstract in *Nickel Bulletin*, 1958, vol. 31, No. 12, p. 339). The use of this coating at temperatures in the range 800°-1200°C. is associated, however, with certain problems caused by differences in the properties of the metals involved. Tests showed that (1) heating at 800° or 1000°C. frequently, but not consistently, resulted in the formation of blisters between the chromium and nickel layers; (2) prolonged heating weakened the bond between the nickel and chromium layers; and (3) thermocycling between room temperature and 800° or 1000°C. caused the nickel to separate from the chromium, principally at sharp edges or corners. An investigation of these interrelated problems is reported in the present paper.

Blister formation was eliminated, and edge separation reduced slightly, by improvements in the treatment of the chromium surface prior to nickel plating. The weakening of the bond between the nickel and chromium layers appears, however, to be inherent in the coating system.

Ductility of Nickel Coatings

H. J. READ and T. J. WHALEN: 'The Ductility of Plated Coatings.'

46th Ann. Tech. Proc., Amer. Electroplaters' Soc., 1959, pp. 318-25; disc., p. 388.

In the first section of the paper the authors give a detailed description of a bulge-test apparatus employed to determine the ductility of electrodeposited coatings and outline the methods used in preparing specimens for testing. Data obtained in such tests are discussed in the last section of the paper.

The experimental study, carried out both on stripped nickel coatings deposited from Watts, chloride and fluoborate solutions and on composite specimens (i.e., deposit+basis metal), has indicated the influence, on ductility, of the following variables: basis metal, deposit thickness, strain rate, and the time between deposition of the coating and testing.

It is concluded that the ductility of plated coatings is influenced by the nature of the basis metal, the thickness of the deposit, and (in the case of composite specimens) by the thickness of the basis metal. Strain rate, pinholes, and the period between deposition and testing had little or no effect on ductility.

Relationship between Brightness and Structure in Electrodeposited Nickel

R. WEIL and R. PAQUIN: 'The Relationship between Brightness and Structure in Electroplated Nickel.'

Jnl. Electrochemical Soc., 1960, vol. 107, Feb., pp. 87-91.

Previous investigations of the relationship between the light-reflecting property (brightness) and the structure of electrodeposits have led to the formulation of two theories. According to one, electrodeposits are bright if their microstructure consists of crystallites smaller than the wavelengths of visible light (i.e., smaller than 0·4μ); it has, however, been shown that not all very-fine-grained deposits are bright. The other theory (that the more oriented the grain structure, the brighter is the deposit) has also been disputed. The study now described was undertaken to determine the structural features governing brightness.

Nickel coatings about 50μ thick, and ranging in brightness from dull-grey to specular, were deposited on copper or steel basis metals from Watts solutions containing various addition agents. The microstructures of the as-plated surfaces were examined by electron microscopy, and the fibre axis of the deposits was determined by X-ray diffraction. Brightness was assessed using a photocell to measure light-reflecting properties.

The data obtained confirm previous reports, in that, whereas all the bright deposits were found to have a very-fine-grained structure, some of those which were fine-grained exhibited surface crevices and were therefore not bright. A linear relationship was established between the fraction of the surface area with a roughness less than 0·15μ and the logarithm of light reflected. No direct relationship exists between the degree of preferred orientation and brightness. The fibre axis is, however, related to the type of structure observed (i.e., platelet, equiaxed crystallite, or spiral-type) and the addition agents in the plating solution.

Corrosion Testing of Electrodeposited Coatings

F. L. LAQUE: 'Corrosion Testing of Electrodeposited Coatings.'

46th Ann. Tech. Proc., Amer. Electroplaters' Soc., 1959, pp. 141–8.

In this paper the author reviews the three main types of test used to evaluate the corrosion-resistance of electrodeposits : atmospheric-exposure tests, accelerated-corrosion tests, and tests designed to throw light on corrosion mechanisms. The aim and main features of the first two types of test are outlined, their advantages and limitations are summarized, and attention is drawn to the factors influencing the validity of the results obtained. In the final section of the paper a survey is given of the types of test which have been used to study the basic principles underlying the corrosion behaviour of electrodeposited coatings.

Corrosion Testing of Electrodeposits by Means of the 'Corrodkote' Test

D. M. BIGGE: 'Experience With the Use of the 'Corrodkote' Test.'

46th Ann. Tech. Proc., Amer. Electroplaters' Soc., 1959, pp. 149–53; disc., pp. 369–70.

The inability of the neutral salt-spray corrosion test to provide a reproducible and reliable assessment of the service performance of plated parts exposed on cars prompted the Research Committee of the American Electroplaters' Society to establish Project No. 15 'to develop a suitable accelerated test for decorative protection by plating steel and zinc-base alloy for use outdoors'. The Committee examined more than twenty different procedures, some new, some already in use, one of which, the 'Corrodkote' test, was evaluated in the laboratories of the Engineering Division of Chrysler Corporation.

This paper outlines the work which led to the development of the optimum slurry composition (Formula No. 59), and gives details of the test programme carried out to determine the degree to which the accelerated-test results were relevant to the actual service performance of the plated components.

Application of Formula No. 59 (see composition below) was found to cause corrosive attack considered typical of that resulting from exposure of a plated component to the Detroit environment. Graphs presented illustrate the high degree to which the performance of (copper)/nickel/chromium-plated automobile parts (as assessed by 20 hours' exposure to the 'Corrodkote' test) was reflected in the performance of similar parts after one year's exposure on a stationary site, and after one year's actual service on cars: on the basis of this correlation, the Chrysler Corporation has now incorporated the test into their acceptance procedure for plated parts.

Formula No. 59

$Cu(NO_3)_2.3H_2O$	0·035 g.
$FeCl_3.6H_2O$	0·165 g.
NH_4Cl	1 g.
Water	50 ml.
Kaolin	30 g.

Sulphur-Dioxide Accelerated-Corrosion Test: Conditions and Equipment

J. EDWARDS: 'Sulfur Dioxide Accelerated Corrosion Test: Testing Conditions and Equipment.'

46th Ann. Tech. Proc., Amer. Electroplaters' Soc., 1959, pp. 154–8; disc., pp. 370–1.

The sulphur-dioxide test has been adopted by a number of industrial firms in Britain as a production-control or acceptance test for plated articles, particularly nickel/chromium-plated steel. Using the test conditions previously recommended, the results obtained have been fairly satisfactory (see abstract of paper by EDWARDS in *Nickel Bulletin*, 1958, vol. 31, No. 3, pp. 73–4), but some doubt remained as to the permissible range of temperature variations. To resolve this doubt, and to carry out the requisite systematic investigation of the effects of varying the temperature of the test atmosphere, it was necessary to provide some means of controlling the temperature within fairly close limits. Such a temperature control, which incurs the difficulty of avoiding the occurrence, within the cabinet, of temperature gradients large enough to cause general condensation on the articles under test, was successfully provided by using a heater of low rating and ensuring that the cabinet was well insulated.

The result of tests carried out with the modified apparatus are presented in the first section of the paper. The second section gives full details of the construction and operation of the test equipment. In the final section the author outlines the scope and applications of the sulphur-dioxide test.

The test conditions now recommended are:

Temperature,	25±2°C.
Relative humidity,	>95 per cent.
Sulphur-dioxide concentration,	1 vol. per cent. (limiting range 0·5–2 per cent.)
Duration of test,	24 hours (for acceptance testing).

Experience with the Copper-Chloride-Modified Acetic-Acid/Salt-Spray Test

C. F. NIXON, J. D. THOMAS and D. W. HARDESTY: 'Experiences with the Copper Chloride Modified Acetic Acid Salt Spray.'

46th Ann. Tech. Proc., Amer. Electroplaters' Soc., 1959, pp. 159–63; disc., pp. 371–3.

The authors' aim is 'to relate some experience with the CASS (copper-chloride-modified acetic-acid/salt-spray) test, taken both from the practice of General Motors Corporation and from that of others, and to supplement briefly that which has been already published concerning its operation'.

A brief outline of the development of the test is followed by a discussion of evidence offered in support of the decision by General Motors to adopt the requirement that decorative plating on the external components of its cars must withstand a minimum of 16 hours' exposure to the 'CASS' test without significant failure. The rôle played by the test in plating research is then illustrated by a description

of its use in experiments conducted to determine the influence of the chromium deposit, and of duplex-nickel coatings, on the corrosion-resistance of composite coatings.

Notes on the operation of the copper-chloride-modified acetic-acid/salt-spray test conclude the paper.

See also

Corrosion-Testing with the Copper-Accelerated Acetic-Acid/Salt-Spray Test

G. L. SUKES: 'Testing Plating Durability: the Copper-Accelerated Acetic-Acid Test.'

Metal Finishing, 1959, vol. 57, Dec., pp. 59–65.

After outlining the requirements demanded of an accelerated-corrosion test by producer and purchaser of plated parts, the author describes the work which led to the development of the copper-accelerated acetic-acid/salt-spray test.

The test conditions are tabulated and the factors governing optimum results are listed. Information in this connexion is supplemented by data indicating (1) acceptance standards recommended for copper/nickel/chromium coatings on steel, zinc-base die castings and aluminium, for nickel/chromium coatings on brass, bronze or copper, for zinc-plated and cadmium-plated steel, and for anodized aluminium; and (2) the method of rating plated or anodized parts on the basis of 'CASS'-test results.

The author ends the paper with a discussion of the advantages of the 'CASS' test and an assessment of its reliability as an acceptance test for plated parts.

Approaches to the Improvement of the Corrosion-Resistance of Decorative Coatings

F. A. LOWENHEIM and W. H. ROWAN: 'Some Aspects of the Corrosion of Decorative Coatings.'

46th Ann. Tech. Proc., Amer. Electroplaters' Soc., 1959, pp. 205–10; disc., p. 379.

As a means of placing in proper perspective the question of corrosion testing in general, and the results presented in particular, the authors, in introducing their subject, draw attention to the limitations of corrosion tests and emphasize the need for care in the interpretation of the data obtained. Three methods of approach are discussed in connexion with the development of electrodeposited coatings of improved corrosion-resistance:

(1) *Tests conducted by the A.S.T.M. B8 Committee*

The data presented relate specifically to that part of the research programme indicating the beneficial effects which result from an increase in the thickness of the final chromium coating in nickel/chromium deposits.

(2) *Statistical Design in Corrosion Testing*

To exemplify the advantages of applying statistical techniques to corrosion testing, the authors outline the use of, and the results obtained from, a 'fractional factorial' design which, entailing tests on only 64 panels, enabled evaluation of the effects of the following six variables: the use of a tin flash prior to copper/nickel/chromium plating; the substitution of 12 per cent. tin bronze for the usual copper undercoat; the presence, and absence, of an intermediate layer of nickel in copper (or bronze)/chromium systems; and (comprising three variables) the use of various types and thicknesses of chromium deposit.

Introduction of a tin undercoat is shown to offer little or no advantage, and might even be deleterious. The bronze undercoat is deemed slightly better than a copper one, and the major contribution of nickel to the corrosion-resistance of composite deposits was found to depend, to a certain extent, on the type of chromium forming the final coating. The beneficial effects of increasing the thickness of the chromium layer was also revealed by the statistical analysis.

(3) *Feasibility of Substituting Other Materials for Copper and Nickel*

The data presented were obtained from a three-year programme of atmospheric tests carried out to evaluate the effects, on corrosion-resistance, of using 12 per cent. tin bronze or copper as undercoats for 0, 0·25 or 0·5 mil of nickel+0·01 mil of chromium. These tests demonstrated the superiority of the bronze undercoat.

Data available after corrosion tests of 4 years' duration confirm the excellent corrosion-resistance of tin-nickel deposits in industrial environments indicated by data discussed in a previous report (see abstracts in *Nickel Bulletin*, 1958, vol. 31, No. 2, pp. 42-3; No. 8, pp. 219-20).

Improvements in the Corrosion-Resistance of Electroplated Die Castings

W. H. SAFRANEK, H. R. MILLER and C. L. FAUST: 'Improved Corrosion-Resistance for Electroplated Die Castings.'

46th Ann. Tech. Proc., Amer. Electroplaters' Soc., 1959, pp. 133–40; disc., p. 368.

In previous work, which, like that now described, was concerned with the feasibility of improving the corrosion-resistance of plated zinc-base die castings, and was conducted at Battelle Memorial Institute under the aegis of the American Zinc Institute, SAFRANEK and FAUST carried out accelerated-corrosion tests on die castings plated with (1) 0·01 mil of chromium over an undercoat of 0·8, 1·3 or 1·6 mils of nickel, or (2) 0·8 mil of nickel+0·08 mil of bright crack-free chromium (see abstract in *Nickel Bulletin*, 1959, vol. 32, No. 1, pp. 9-10). The results indicated the excellent corrosion-resistance conferred by the latter type of composite coating.

In the initial section of the present paper details are given of a one-year programme of atmospheric-corrosion tests which, initiated to determine the validity of the accelerated-test results, confirmed

the superiority of coating (2). The authors then present data, derived from a new programme of accelerated-corrosion tests (using the 'Corrodkote', acetic-acid/salt-spray and copper-accelerated salt-spray techniques), on the basis of which it is anticipated that coatings of the following type will exhibit good corrosion-resistance for at least one year of continuous outdoor exposure at Detroit or Kure Beach:

(*a*) 0·8 mil of bright nickel + 0·025 mil of bright crack-free chromium;

(*b*) 0·8 mil of duplex nickel + 0·01 or 0·02 mil of chromium;

(*c*) 0·03 mil of crack-free chromium + 0·8 mil of bright nickel + 0·03 mil of bright crack-free chromium.

The remainder of the paper is concerned with discussion of the characteristics of bright crack-free chromium deposits, the practical aspects of electrodepositing such coatings, and data confirming the improved corrosion-resistance conferred by duplex-nickel plating. The corrosion performance of duplex-nickel coatings was found to depend upon the brighteners selected for deposition of the first semi-bright nickel layer. The corrosion-resistance conferred by semi-bright nickel with a columnar structure was good; inferior results were obtained when the semi-bright nickel had a banded structure.

Nickel/Chromium Plating of Die Castings

BRIT. NON-FERROUS METALS RESEARCH ASSOC.: 'Better Plating on Die Castings.'
Development Report No. 62.
Issued by the Association, Jan. 1960; 18 pp.

Dissatisfaction with the performance of plated components, especially those exposed on motor cars, has led to a great deal of publicity for methods of improving the corrosion-resistance of nickel/chromium deposits. Attention has been focused, in particular, on the replacement of the normal bright-nickel undercoat by 'duplex nickel' and on the use of so-called 'crack-free chromium'. Work at the British Non-Ferrous Metals Research Association has so far been concerned with the practicability of improving the performance of nickel/chromium deposits by employing the crack-free-chromium processes to increase the thickness of the chromium.* The results summarized in this progress report agree closely with the findings of similar studies in the United States, particularly those sponsored by the American Zinc Institute at the Battelle Memorial Institute. The Association's investigations have been conducted primarily in relation to zinc-alloy die castings, but the findings are considered to be to a large extent applicable also to nickel/chromium plating of other basis metals, such as steel and brass.

In the report reference is first made to data indicating that maintenance of the thickness of the nickel undercoat, as laid down in *B.S.* 1224, will remain a vital factor even after adoption of improved chromium coatings. The advantages of crack-free chromium are then outlined, and notes are given on the general plating requirements for production of such deposits. Corrosion tests illustrating the improvements obtainable by deposition of crack-free chromium are described, and data are presented on the variation in the corrosion-resistance of nickel/chromium deposits with variation in the thickness of the nickel undercoat and the final chromium coating. Comments on three sets of plating conditions capable of producing thicker chromium deposits lead to the final section of the report in which attention is drawn to control tests suitable for determining the thickness of the nickel deposit and the thickness and tendency to cracking of the chromium deposit.

* Parallel investigations of the corrosion-resistance conferred by the 'duplex-nickel' process (which involves deposition of a layer of normal bright nickel over a suitable type of dull or semi-bright nickel) is at present in progress.

Electrodeposition and Corrosion-Resistance of Chromium/Nickel/Chromium Coatings

H. BROWN and M. WEINBERG: 'Outdoor-Corrosion Results with Chromium-Nickel-Chromium Plate.'
46th Ann. Tech. Proc., Amer. Electroplaters' Soc., 1959, pp. 128–32; disc., pp. 367–8.

In the introductory section of the paper the author discusses the results of atmospheric-corrosion tests carried out (in an industrial environment) on zinc-base die castings and steel specimens plated with chromium / nickel / chromium, copper / chromium / nickel/chromium and nickel/chromium/nickel/ chromium coatings. The corrosion behaviour of these composite coatings is compared with that exhibited by copper/nickel/chromium and nickel/chromium deposits of various thicknesses, and the types of corrosion pit associated with each system are discussed and illustrated. Certain of the systems which incorporated a final chromium/nickel/chromium plating sequence (i.e., a 0·05-mil high-temperature-type chromium undercoat + a conventional nickel deposit + a final bright-chromium deposit) are stated to have conferred outstanding protection against corrosion during three years' exposure in a Detroit industrial atmosphere.

The advantages of this system are: (1) it enables the use of the most corrosion-resisting type of dull crack-free chromium coating as an undercoat, and (2) the chromium undercoat tends to divert the corrosion pits laterally along the nickel coating, thus inhibiting their downward penetration into the basis metal and increasing corrosion-resistance, particularly in the recessed areas where the chromium and nickel deposits are thin. Its drawback (which has hindered plating on a production scale) is the problem of rinsing the initial chromium coating thoroughly enough to prevent drainout of chromic acid from blind holes and rack contacts into the main nickel-plating solution.

In the main section of the paper details are given of the plating sequences developed for electrodeposition of chromium/nickel/chromium coatings on zinc-base die castings, steel and stainless steel.

Corrosion of Nickel-plated Mild Steel: Influence of Deposit Orientation

B. C. BANJEREE: 'Corrosion of Nickel-Coated Mild Steel.'

Jnl. Electrochemical Soc., 1960, vol. 107, Feb., pp. 80–6.

Work on the crystal structure and orientations of nickel electrodeposits (see reference to papers by BANERJEE in volumes 31 and 32 of *The Nickel Bulletin*) has shown them to be greatly influenced by variation in plating conditions. In the case of electrodeposited face-centred-cubic metals, it was previously thought that lateral growth (defined by the orientation of the more-densely-packed atomic planes, such as (111), (100), or $(10\bar{1}0)+(211)$, parallel to the substrate surface) confers better protection against corrosion than out-growth (defined by (110) or (210) orientations). The results now reported by the author do not support this assumption.

Mild-steel discs electroplated with nickel deposits exhibiting (100), $(10\bar{1}0)+(211)$, (110), or (210) orientations were exposed to 0·5 per cent. hydrochloric-acid and 5 per cent. sodium-chloride solutions at 25°C. Determination of the rate of dissolution of iron showed that in the hydrochloric-acid solution the greatest protection was conferred by the deposits with (210) orientation. In the neutral sodium-chloride solution no significant difference was observed in the dissolution rates associated with the various orientations.

The results are discussed in relation to the precipitation of basic iron salts, the electrochemical anisotropy of different faces of a single crystal, and the texture of the deposits.

Influence of the Basis Metal on the Corrosion-Resistance of Nickel Coatings

M. H. JONES, C.-Y. LU, A. F. MOHRNHEIM and J. ZAJDOWSKI: 'The Influence of the Physical Metallurgy and Mechanical Processing of the Basis Metal on Electroplating. VI. Ferrous Metal Conditions Affecting the Durability of Watts Nickel Deposits.*

46th Ann. Tech. Proc., Amer. Electroplaters' Soc., 1959, pp. 113–21; disc., p. 367.

This report summarizes the results of five years' work carried out, within the scope of A.E.S. Research Project No. 14, to study the influence, on the corrosion-resistance of nickel electrodeposits, of the variables associated with the nature of a ferrous basis material and the preparation of its surface prior to plating.

*For abstract of Part V see Nickel Bulletin, 1959, vol. 32, No. 2, pp. 42-3.

The factors studied, and the scope of the test programme associated with each, are noted below.

(1) *Influence of Non-Metallic Inclusions*

The effects of semi-conducting inclusions were determined on a rimming steel in which the inclusions present were mainly of the manganese-ferrous-sulphide type. The influence of non-conducting inclusions was studied using electrolytic iron containing silica particles.

(2) *Influence of the Basis Metal*

The corrosion-resistance of Watts-nickel deposits was evaluated as a function of the variation in the nature, inclusion content and metallurgical history of the twelve ferrous materials which were used as basis metals in this phase of the programme.

(3) *Influence of Mechanical Polishing Prior to Plating*

The effects of polishing the basis metal prior to plating were assessed in terms of the relative corrosion-resistance exhibited by nickel-plated low-carbon-steel specimens when subjected to different types of surface-finishing treatment.

(4) *Influence of Stretching the Basis Metal Prior to Plating*

Corrosion tests were conducted on aluminium-killed deep-drawing steel nickel plated in the as-rolled or rolled-and-annealed condition. Account was taken also of the influence of polishing before and after rolling.

In the present work two methods were employed to relate basis-metal effects to the corrosion-resistance exhibited by the nickel coatings. In the first, a microscopical technique was used directly to correlate surface defects in the basis metal with the pits that developed in the nickel deposits after corrosion testing. To evaluate the effects of deformation and of different types of polishing, recourse was had to statistical techniques by which cause and effect were correlated in an indirect way. In the first method corrosion-resistance was evaluated by means of the Pierce-Pinner electrochemical test, the carbon - dioxide - saturated - hot - water test, the acetic-acid/salt-spray test, or outdoor-exposure tests. In the second approach the acetic-acid/salt-spray test or the 'Corrodkote' test was employed as a criterion of corrosion-resistance.

The results presented show that while certain of the basis metals can differ greatly in their effects on the corrosion-resistance of the deposits, such differences become less significant with increase in the thickness of the coating. At a deposit thickness of 0·5 mil, the effects of the basis metal were, to a certain extent, related to inclusion content, though the degree to which non-metallic inclusions acted as corrosion-pit initiators depended on their type and size. Non-conducting inclusions, such as silica or alumina, contributed more to failure of the nickel coating than semi-conducting inclusions of the sulphide type.

In the case of deposits 1 mil thick, the type of surface finish was also found to affect corrosion-resistance. The influence of the polishing treatment appeared, however, to vary with the nature of the corrosive environment, and although the results of the acetic-acid/salt-spray test and the 'Corrodkote' test reflected a similar pattern in the effects of different commercial treatments, the latter test was far more sensitive to the variations involved. The data derived from the 'Corrodkote' test indicate that the effects of greased-belt polishing are more beneficial, at equivalent surface roughness, than those of dry-belt polishing. Corrosion-resistance associated with fine finishes (10 μ in.) was superior to that with coarse (40 μ in.), and, in general, the resistance obtained with coatings deposited on surfaces prepared in the laboratory by hand polishing was higher than that of nickel-plated surfaces prepared by commercial-belt polishing.

At the 1-mil level the performance of the deposit was affected by the degree of extension suffered by the various basis metals prior to plating. Effects in this connexion were most pronounced at high elongations (20–40 per cent.), and, as before, the acetic-acid/salt-spray test and the 'Corrodkote' test were found to differ in the sensitivity with which they detected differences between the various treatments. The data derived from the acetic-acid/salt-spray test demonstrated that polishing before a 30–40 per cent. elongation resulted in significantly higher corrosion rates than those determined when polishing followed extension. Corrosion-resistance was moreover affected by the direction of polishing before extension: polishing transverse to the stretching direction was more detrimental than longitudinal polishing. The authors conclude that the effects of stretching are related primarily to the surface condition of the basis metal.

Electrolytic Purification of Nickel-Plating Solutions

A. M. MAX and M. L. WHITEHURST: 'The Effect of Flow Rate and Current Density on the Electrolytic Removal Rate of Iron and Copper From a Watts Nickel Solution.'

46th Ann. Tech. Proc., Amer. Electroplaters' Soc., 1959, pp. 181–7; disc., p. 377.

When considered in the light of control requirements, electrolytic purification of plating solutions assumes particular significance, since the procedure is particularly adaptable to continuous purification. The work outlined by the authors was conducted to extend the range of information available on electrolytic purification, and, in particular, to study the factors involved in the removal of two elements (copper and iron) of special relevance to the Watts nickel-plating solution. The two sections of the paper are concerned, respectively, with the theoretical aspects of electrolytic purification and with presentation of data derived from the experimental investigation.

The removal of copper and iron, from a Watts solution operated at 140°F. (60°C.), was studied as a function of flow rate (which was varied in the range 6–50 ft./min. (1·8–15 m./min.)) and current density (which ranged from 0·5 to 16 amp./sq. ft. (0·05 to 1·73 amp./dm.²)). The concentration of ferrous sulphate and copper sulphate present at the beginning of each run was approximately 50 mg./L. Mathematical models are proposed which permit the interpretation of the data obtained and the translation of depletion data to other sets of conditions.

Deposition of copper in the nickel solution was governed by its diffusion rate through the cathode film. The diffusion rate was found to increase materially with increase in the rate of flow, but current density was apparently a negligible factor in this respect. The surface area of the cathode played an important rôle: the cathode surface becomes rough as deposition continues, the cathode area increases, and consequently the rate of copper depletion also increases.

The experiments on iron removal indicate that there is a threshold current density below which the metal is not deposited: no iron was removed at a current density of 4 amp./sq. ft. (0·43 amp./dm.²) or less, and for definite removal a current density of 16 amp./sq. ft. (1·73 amp./dm.²) was needed. At the latter level an increase in the flow rate increased the rate of iron removal.

Electrolytic removal of iron was complicated by the low solubility of ferric hydroxide at a pH higher than 3. It is anticipated that, under the oxidizing conditions present in most plating installations, conversion of iron to ferric hydroxide will occur at this pH level.

The removal of copper and, over a limited range, of iron is shown to follow a logarithmic decay curve.

Influence of Storage on the Soldering Characteristics of Tin and Tin-Alloy Coatings Deposited over Copper or Nickel Undercoatings

C. J. THWAITES: 'The Solderability of Some Tin, Tin Alloy and Other Metallic Coatings.'

Trans. Inst. Metal Finishing, 1959, vol. 36, Winter, pp. 203–19.

In its many different industrial applications, soft soldering is usually facilitated by pre-coating the surfaces to be joined with a metal which is easily wetted by the molten solder. In the case of tin and certain other metallic coatings, however, difficulties occasionally arise when, after periods of storage, the surfaces are not readily wetted by the solder, a defect which is most frequently experienced with coatings applied by electrodeposition. The study now reported was initiated to determine the influence of storage on the soldering characteristics of various types of coating.

Three groups of coating were selected for study: hot-dipped or electrodeposited tin coatings, some of those electrodeposited being subsequently flow-melted

or flow-brightened by heat-treatment; tin-alloy coatings (i.e., tin-zinc, tin-lead, tin-nickel, tin-cadmium electrodeposits); and electrodeposited cadmium or silver coatings. In general, each coating was applied, at three levels of thickness (0·00005, 0·0001, 0·0003 in.: 0·00125, 0·0025, 0·0075 mm.), onto steel, brass and copper basis metals. The pure tin coatings were given three different types of protective post-treatment (passivation, deposition of a layer of resin, and deposition of a hard resin-base lacquer).

The influence of the following three types of undercoating was studied: electrodeposited nickel; electrodeposited copper; and (under a tin deposit produced from a stannate solution) 12 per cent. tin-bronze. The undercoatings were deposited to a thickness of 0·0001 in.

Immediately after deposition of the coating, and at the end of each of the five periods (comprising a total of two years) for which they were stored at 25° and 50°C., all the samples were subjected to a 'spread-of-drop' test*. Altogether over 8,000 specimens were tested during the investigation. Many specimens were metallographically examined to obtain information on the formation and growth (due to diffusion during storage) of intermetallic-compound layers. The results of the study are presented *in extenso*. The salient findings are quoted below.

'(1) Coatings of tin or alloys of tin with lead, zinc or cadmium generally give excellent initial solderability, and retention of solderability, when not less than 0·0003 in. (0·0075 mm.) thick.

'(2) Hot-dipped tin coatings are pre-eminent for soldering quality.

'(3) If solderability is the only criterion, tin-alloy coatings have no advantage over pure tin.

'(4) There is no decrease in the solderability of coatings on steel when they are applied correctly and stored under reasonable conditions.

'(5) With a brass basis, deterioration in the solderability of electrolytic coatings may occur after storage, due to zinc diffusion and subsequent action of atmospheric moisture when storage conditions are unsuitable. A 0·0001-in. (0·0025-mm.) thick copper undercoat beneath electroplated tin or alloy coatings, or a 0·0001 in. thick nickel layer under hot-dipped tin coatings, alleviates this difficulty. In the latter case, contamination of the dipping bath by zinc is also prevented.

'(6) A copper basis leads to decrease in solderability due to loss of coating as tin-copper intermetallic compound, but this loss is only serious for coating thicknesses less than 0·0003 in. (0·0075 mm.).

'(7) A 0·0001-in. thick nickel undercoat gives enhanced initial solderability and no deterioration in storage of adequately thick coatings, but the final coating should be applied without any delay.

'(8) A 0·0001-in.-thick copper undercoat generally enhances initial solderability of steel and brass, but decrease in solderability of thin coatings occurs, as mentioned in (6), for plating direct on a copper basis.

'(9) Flow-melted tin coatings show slightly superior storage properties, compared with as-plated coatings of a similar thickness, when both are on copper. On steel and brass, there appears to be no advantage in flow-melting.

'(10) Where the coating system has to be chosen for reasons other than the simple attainment of good solderability, and the possibility of deterioration has to be faced, storage should be at ambient temperature, or preferably at 25°C., to prevent condensation, and it should be for the minimum possible period. This recommendation applies particularly to brass and copper work. Humidity and atmospheric contamination should be kept low, perhaps by storing the coated work in inert containers containing a desiccant.'

* In which the area of spread of a fixed volume of solder is determined as a criterion of solderability

NON-FERROUS ALLOYS

Constitution of the Nickel-Molybdenum-Aluminium and Nickel-Molybdenum-Silicon Systems

R. W. GUARD and E. A. SMITH: 'Constitution of Nickel-base Ternary Alloys. I. Nickel - Molybdenum - Aluminium System. II. Nickel-Molybdenum-Silicon System.'

Jnl. Inst. Metals, 1960, vol. 88, Feb., pp. 283–5; 285–7.

The data reported in this paper were derived as part of a series of investigations undertaken to establish phase relationships in nickel-base systems involving aluminium and silicon compounds. The compounds Ni_3Al and Ni_3Si are important constituents of some high-temperature alloys, and it was hoped that the data obtained would contribute to the development of improved materials. With the same aim in mind, the third element of the system was selected from metals commonly used as alloying additions in nickel-base heat-resisting alloys.

Part I of the paper presents the results of a study of the nickel-rich portion of the nickel-molybdenum-aluminium constitutional diagram. The phase relationships at 1175°C. were investigated and the solvus for the γ solid solution was determined at 900°C. A ternary compound designated ψ was found in the vicinity of nickel 58, molybdenum 7·5, aluminium 34·5, at. per cent. Its existence was confirmed by the presence of a new set of X-ray diffraction lines, but the structure, which is complex, was not determined. None of the binary compounds Ni_3Al, NiAl, or NiMo shows appreciable solubility in the ternary section.

In Part II, details are given of the nickel-molybdenum-silicon system. The ternary section was

established at 1100°C. and the γ solvus line was determined for 900°C. A ternary compound ψ was found at nickel 50, molybdenum 32, silicon 18, at. per cent. X-ray-diffraction studies confirmed the metallographic evidence for its existence, but its structure was not determined.

Despite the similarity between Ni_3Si and Ni_3Al, their relationships in the nickel-molybdenum-aluminium and nickel-molybdenum-silicon diagrams were found to show important differences. These differences are related to: (1) the introduction, in the latter case, of a highly stable ternary compound ψ which limits the region over which molybdenum appears in the diagram, and (2) the large difference in the size of the aluminium and silicon atoms, which changes their compound-formation behaviour. The change in solubility of Ni_3Si and Ni_3Al in nickel solid solutions is affected in a similar degree by molybdenum additions. The equilibrium amount of compound that can be precipitated at a given temperature is similar for both. Neither compound shows any tendency to take molybdenum into solution.

Influence of Nickel Additions on the Oxidation Behaviour of Copper

F. BOUILLON and J. STEVENS: 'Influence of Small Amounts of Nickel on the Oxidation of Copper.' *Acta Metallurgica*, 1959, vol. 7, Dec., pp. 774–6.

The mechanism underlying the growth, on metals, of thin continuous oxide films (20–1000Å thick) is little understood. The experiments described were carried out to determine the influence of small alloying additions of nickel on the behaviour of copper exposed, at temperatures up to 200°C. and at atmospheric pressure, to pure oxygen. It was hoped that the nickel additions would induce the formation of mixed oxides, which, influencing the migration of metal ions towards the oxide/gas interface, would thus throw light on the reactions involved.

The five alloys prepared for investigation contained, respectively, 0·1, 0·5, 1, 5 and 10 wt. per cent. of nickel. After homogenization treatment the specimens were electropolished and then oxidized.

No nickel oxide was determined during metallographic and analytical examination of the oxide films formed at 150°, 185° and 200°C. The following are the main findings with respect to the influence of the nickel additions on the oxidation-resistance of copper:

(1) The copper-nickel alloys containing 5 and 10 per cent. nickel oxidized less rapidly than pure copper during the period studied.

(2) Alloys with nickel contents of 0·5 and 1 per cent. oxidized more rapidly than copper during an initial period of exposure, the duration of which varied inversely with the nickel content.

(3) The rate of oxidation of the specimens containing 0·1 per cent. of nickel was the highest exhibited over the period studied.

(4) The oxide CuO formed sooner on the alloy specimens than on the pure copper.

Penetration of Alloys by Liquid Metals and Salt Melts

See abstract on p. 90.

Improved Nickel-containing Gunmetal for Quality Castings

A. M. PATTON: 'An Improved Nickel-containing Gunmetal for the Production of High-Quality Castings.'*

Brit. Foundryman, 1960, vol. 53, Feb., pp. 82–7.

For many years numerous bronze founders have held the view that the addition of small amounts of nickel improves the properties of bronzes and gunmetals, particularly in large sections. This improvement has been attributed both to better feeding of the sections and, in the case of leaded alloys, to refining of the coarse interdentritic lead segregates. There has, however, been little critical study of the subject until the recent work of HUDSON, WOOD and GREGG, which demonstrated the beneficial effect of the addition of 2 per cent. of nickel to some of the standard bronzes: see abstract in *Nickel Bulletin*, 1958, vol. 31, No. 12, pp. 320–1. Their researches led to the suggestion that an alloy containing tin 6–7, zinc 3–4, nickel 1·5–2·5, per cent., remainder copper, might prove to have good mechanical properties, combined with pressure-tightness and far less susceptibility to the pronounced decrease in properties, which, in the standard bronzes, occurs with increase in section size. The work now described, carried out to verify this hypothesis, has demonstrated that the initial promise of this alloy has been fully realized.

The basic designs of the step-bar and wedge castings employed in the study were the same as those used by HUDSON *et al.*, but the range of section sizes was extended, by the use of smaller castings, to include not only sections of ½–3 in. (1·25–7·5 cm.) but also smaller sections varying from $\frac{3}{16}$ to ½ in. (0·5–1·25 cm.). Two sizes of the keel-bar type of mould were also made. One large and one small wedge, one large and one small step-bar, and a small keel-type test bar were cast from each of the two heats of improved gunmetal melted. Feeding characteristics were assessed by casting one large keel-bar from the improved alloy and from gunmetals of the following type: 85-5-5-5, 83-5-5-5+ 2 per cent. nickel. Specimens for tensile and Izod-impact testing were sawn from the smaller castings,

* See also *Publication 1885* of The Mond Nickel Company, Ltd., 'Improved Gunmetals for Quality Castings': abstract in Nickel Bulletin, 1959, vol. 32, No. 12, p. 356.

and specimens for microexamination, hardness testing, and density determinations were taken from positions adjacent to the specimens used for impact testing.

The following conclusions are drawn from the data presented:

'This improved alloy should prove of great value to the user of gunmetal castings, either as an addition to the range of foundry alloys, or as a replacement for some of the standard types. Not only has the new material an ultimate tensile strength in thin sections which is only surpassed by that of the more expensive 88-10-2 alloys, but it has a 0·1 per cent. proof stress greater than that obtainable from any of the currently used gunmetals. It is also evident, from the trials in the foundry, that it is as amenable to the production of pressure-tight castings as is 85-5-5-5 gunmetal.

'A further property which makes the alloy attractive to the designer is its lessened sensitivity to changes of section size, as compared with standard alloys.

'The following percentage compositional specification is tentatively suggested for the new alloy: tin 6–7, zinc 3–5, lead 3–5, nickel 1·5–2·5, per cent., phosphorus not greater than 0·02 per cent. in castings over 1 in. in section, remainder copper.

'The tensile strength of castings made from this alloy should be about 18 tons/sq. in. (28·5 kg./mm.^{2}) in separately cast test bars, and not less than 14 tons/sq. in. (22 kg./mm.^{2}) in fully-fed sections of up to 4 in. (10 cm.) thickness.'

Nickel-Beryllium Casting Alloys

'Beryllium-Nickel Casting Alloys.'

Materials in Design Engineering, 1960, vol. 51, Jan., p. 11.

In this short note reference is made to data tabulated on the physical and mechanical properties of two age-hardenable nickel-beryllium casting alloys (see composition below) developed by Brush Beryllium Company.

Alloy	*Be*	*C*	*Ni*
	%	%	%
'220-C'	2·00–2·30	0·40 max.	Bal.
'260-C'	2·55–2·80	0·40 max.	Bal.

The lower beryllium content of the '220-C' alloy, though associated with a moderate decrease in hardness and strength, results in improved machinability. Both alloys are magnetic and are characterized by high strength, hardness and corrosion-resistance; they exhibit excellent resistance to temperatures up to the region of 800°F. (425°C.).

The alloys, which may be cast by various techniques, are used in such applications as turbine wheels, glass moulds, plastic-compression moulds, textile needles, valve bodies, wrench drills and fuel-injection tips.

Titrimetric Determination of Nickel in Non-Ferrous Alloys

See abstract on p. 70.

Determination of Nickel and Cobalt in Alloys

See abstract on p. 70.

NICKEL-IRON ALLOYS

Chemical Cleaning of Oxidized Nickel-Iron-Cobalt Alloys for Glass-to-Metal Seals

N. RAIN: 'Chemical Cleaning of Oxidized Nickel-Iron-Cobalt Alloys for Glass-to-Metal Seals.'

Jnl. Scientific Instruments, 1959, vol. 36, Nov., p. 479.

During the production of glass-to-metal seals, alloys of the nickel-iron-cobalt type (e.g., 'Nilo K', 'Kovar') become heavily oxidized, and it is necessary to remove this oxide to enable further processing, such as electroplating, to take place. It is not easy to remove the oxide without appreciable attack on the underlying metal, but in this short note the author outlines a treatment which has proved effective and reliable when used for this purpose.

After degreasing, the glass-to-metal seal is immersed in *Solution* 1 (see below) until the metal is shown to be free from oxide (the time of immersion varies from 10 to 60 minutes depending on the thickness of the oxide). Rinsing in a chromic-acid solution will then remove any smut which might still remain. Measurements on unoxidized 'Nilo K' exposed to the solution at 75°C. revealed a metal loss from the surface of 0·0004 in. (0·01 mm.) per hour.

The addition of nitric acid to *Solution 1* provides an etchant which produces a bright finish on oxide-free 'Nilo K'. This etchant (see *Solution* 2 below) has found application not only as a cleaning pickle for nickel-iron-cobalt alloys prior to glass sealing, but also as an etchant for nickel components requiring an etched surface. The optimum solution temperature is 60°C., and the reaction is fairly vigorous: at this temperature 0·001 in. (0·025 mm.) of alloy per minute is lost from the surface. Immersion for ten to thirty seconds is usually sufficient to produce a clean bright finish, and, in this case also, smut may be subsequently removed by a chromic-acid dip.

Solution 1

Ferric ammonium sulphate ..	50 g.
Sulphuric acid 1·84	125 ml.
Hydrochloric acid 1·16	150 ml.
Water	to make 1 litre
Temperature	60°–80°C.

Chromic-Acid Solution

Chromium trioxide	.. ..	100 g.
Sulphuric acid 1·84	.. ..	30 ml.
Water		to make 1 litre

Solution 2

Ferric ammonium sulphate	..	50 g.
Sulphuric acid 1·84	.. ..	125 ml.
Hydrochloric acid 1·16	.. ..	150 ml.
Nitric acid 1·42 ..	.. ..	150 ml.
Water		to make 1 litre

CAST IRON

Influence of Section Size on the Properties of Grey-Iron Castings

R. C. BATES: 'How Section Size Affects Gray-Iron Castings.'

Materials in Design Engineering, 1960, vol. 51, Feb., pp. 100–2.

Foundry experience has indicated that the mechanical properties of iron castings vary considerably with the section size of the casting, and that, unless information is available on the effects of section size, the use of separately-cast test bars of standard size and design can cause designers and engineers to overestimate tensile strength or underestimate machining difficulties. In the work summarized by the author, an attempt was made to obtain data relevant to irons conforming to the requirements of Classes 20, 30, 40 and 50 of *A.S.T.M. Specification A.45*: see table below.

Six sizes of arbitration bar, ranging in diameter from ¼–3½ in. (0·6–8·5 cm.), were cast. The ultimate strength of specimens cut from the lower half of the bars was determined, and hardness measurements were also carried out. The surface and centre of each bar were subjected to micrographical examination and the type and size of the graphite present were assessed. The data obtained are summarized in the form of curves relating tensile strength and Brinell hardness to section size, to graphite type and size, and to the percentage of carbide present.

The strength and hardness of the arbitration bars is shown to decrease as section size increases. The rate of decrease is high in small bars, but the curve tends to level off in bars 1·5–2 in. (3·5–5·0 cm. in diameter. The curves obtained are of similar shape, but vary in the magnitude of the ordinates. All of them demonstrate that, in the case of the larger-diameter bars, strength and hardness varied only slightly with change in section size.

In bars less than 1 in. (2·5 cm.) in diameter a small decrease in diameter significantly increases tensile strength and hardness (in the one exception, the ¼-in.-diameter bar, the drop in strength was probably associated with the presence of large amounts of free carbide and/or fine graphite in the microstructure).

If more than approximately 3 per cent. massive carbide is present in the microstructure, hardness is not considered a suitable criterion by which to assess the machinability of ferritic, pearlitic, or acicular grey cast iron, and if extensive machining is to be carried out, a section size associated with the presence of more than 5 per cent. massive carbide should be avoided.

Carbide content can be controlled also by modifying the composition of the iron: the carbide content is increased by addition of chromium, or by lowering the carbon equivalent, and is decreased by the addition of copper or nickel.

Composition of Grey Cast Irons

(*See abstract above*)

A.S.T.M. A48 Class No.	C %	Si %	Mn %	S %	P %	Cu %	Ni %	Mo %	Cr %
20	3·41	2·23	0·65	0·12	0·21	—	—	—	—
30	3·19	1·54	0·65	0·11	0·10	—	—	—	—
40	3·24	1·56	0·61	0·09	0·12	1·61	0·68	—	—
40	3·20	1·64	0·62	0·10	0·10	—	0·65	0·47	—
40	3·20	1·92	0·65	0·09	0·10	—	—	—	0·88
50	3·20	1·64	0·58	0·10	0·10	—	2·28	0·92	—

Microstructural Changes During Tempering of Nickel-Chromium White Iron

J. R. MIHALISIN and R. D. SCHELLENG: 'Microstructural Changes upon Tempering Nickel-Chromium White Iron at 400°F.'

Modern Castings, 1960, vol. 37, Jan., pp. 32–5.

The study described was carried out on a white cast iron, of the following nominal composition, selected as representative of the martensitic grades used extensively in applications requiring high abrasion-resistance: carbon 3·3, silicon 0·5, manganese 0·5, nickel 4·5, chromium 2, per cent. (The structure of such irons consists of large amounts of massive carbide in a matrix rendered martensitic in the as-cast condition by the alloying additions: the composition of the iron is modified to satisfy the requirements of the specific application.) Such irons are usually tempered for about 4 hours at 400°F. (205°C.), a treatment which has been found considerably to improve toughness without significantly affecting wear-resistance. The study reported by the authors was conducted in an attempt to throw light on the microstructural changes associated with the heat-treatment.

No marked differences were observed between the microstructures of the as-cast and the tempered material when examined by light microscopy. When, however, the etched microstructures were viewed under polarized light, with an analyzer perpendicular to the polarizer, the martensite plates in the tempered material appeared light, while the martensite in the as-cast sample appeared dark.

Electron microscopy revealed that tempering at 400°F. (205°C.) for 5 hours had caused a lamellar precipitation (within the martensite plates) of a second phase which electron-diffraction analysis showed to be ε carbide. The precipitation of this phase during tempering permits relaxation of the highly-strained tetragonal lattice of martensite and the formation of cubic martensite, a mechanism which is postulated as the cause of the increase in the toughness of the tempered material.

CONSTRUCTIONAL STEELS

Study of Hexagonal Carbide and Nitride Phases Present in Steels

K. W. ANDREWS and H. HUGHES: 'Hexagonal Carbide and Nitride Phases.'

Iron and Steel, 1959, vol. 32, Dec. 18, pp. 654–8.

In the course of their study of carbides and nitrides electrolytically isolated from steels, the authors have encountered a number of hexagonal carbide and nitride phases which, although capable of varying considerably in composition, appear to be isomorphous with Mo_2C, Fe_2N and several other carbides or nitrides of pure transition metals. In the first section of this paper a summary is given of the data available on carbides and nitrides of this type. Information is then presented on twenty-three isomorphous phases which, isolated from alloy steels, were found to contain carbon and/or nitrogen and varying amounts of metallic elements (though it was difficult to elucidate completely the composition of the phases since they invariably occurred in association with other constituents). In certain steels, phases of the type studied have been shown to play an important rôle in the early stages of a precipitation or carbide reaction, and may be a significant factor in relation to precipitation hardening.

Data available on the lattice parameters of binary, ternary and more complex hexagonal nitrides and carbides are listed in the introductory section of the paper. The main section of the paper is concerned with twenty-three carbide and nitride phases isolated from nickel-chromium-molybdenum, nickel-chromium - molybdenum - vanadium, chromium - molyb - denum, chromium - molybdenum - vanadium and chromium-nickel experimental steels covering a wide range of composition. The steels are listed according to their origin, variations in composition, or heat-treatment. The general nature of the hexagonal M_2X-type carbides and nitrides is considered and possible solid-solution effects are discussed.

Low-Temperature Fatigue Properties of Nickel-Chromium-Molybdenum Steel

A. S. KENNEFORD and R. W. NICHOLS: 'The Fatigue Properties at Low Temperatures of a Low-Carbon and an Alloy Steel.'

Jnl. Iron and Steel Inst., 1960, vol. 194, Jan., pp. 13–18.

Whilst several workers have studied the effect of low temperatures on the fatigue properties of unnotched steel specimens under simple reversed stressing, fatigue involving loading cycles and the presence of stress raisers has been the subject of only limited study. The work reported was conducted to determine the influence of these two factors on the low-temperature fatigue characteristics of a free-cutting mild steel and a low-alloy steel of the following composition: carbon 0·29, silicon 0·27, manganese 0·59, sulphur 0·049, phosphorus 0·034, nickel 2·44, chromium 0·74, molybdenum 0·52, per cent.

The two materials were obtained in bar form (cold-drawn in the case of the mild steel, hot-rolled-and-annealed in the case of the alloy steel). Before being machined into test pieces, the mild steel was normalized from 950°C.; the alloy steel was oil-quenched from 950°C. and tempered for 1 hour at 670°C.

Notched and unnotched specimens of each steel were subjected to fatigue tests under zero-mean (tension/compression) and zero-minimum (tension/zero) stress at +20°, −60° and −186°C. Impact and tensile tests were also carried out at room temperature and sub-zero temperatures.

The fatigue endurance limit of both notched and unnotched specimens of the two steels was found to

increase, irrespective of the type of stressing, as the temperature decreased; the endurance ratio (fatigue limit/U.T.S.) remained constant. In the case of the alloy steel, the notch-sensitivity, as measured by the effective stress-concentration factor (fatigue limit (unnotched)/fatigue limit (notched)), decreased slightly with temperature. For the mild steel, notch-sensitivity decreased when the steel was subjected to alternating tension (zero-minimum stress), but increased under tension/compression stressing (zero-mean stress). The severe embrittlement of the mild steel in both tensile and impact tests at −196°C. was not reflected in the fatigue endurance limit.

Influence of Shot-Peening on the Fatigue Strength of Chromium-Plated High-Strength Steel

C. WILLIAMS and R. A. F. HAMMOND: 'The Effect of Shot Peening and of Grinding on the Fatigue Strength of Chromium-Plated High-Strength Steel.'
46th Ann. Tech. Proc., Amer. Electroplaters' Soc., 1959, pp. 195–204; disc., pp. 377–8.

Previous investigations have revealed that shot-peening of low-strength steels prior to chromium plating prevents the reduction in the fatigue limit which is known otherwise to result from chromium plating. The investigation now reported was initiated (1) to determine whether shot-peening would have the same beneficial effect in the case of high-strength steels and, if so, whether these benefits would be counteracted by the effects of low-temperature baking to eliminate hydrogen embrittlement; and (2) to establish the intensity and distribution of internal stress in shot-peened steel, the degree of surface roughness induced by peening, and the effect, on the fatigue strength, of grinding (either before or after plating) to eliminate the peening texture.

Two steels were selected for study: a 2½ per cent. nickel-chromium-molybdenum steel (En25) heat-treated to an ultimate strength of 180,000 p.s.i. (80·5 t.s.i., 126·5 kg./mm.²) and a 1¾ per cent. nickel-chromium-molybdenum steel (A.I.S.I. 4340) heat-treated to a strength of 224,000 p.s.i. (100 t.s.i., 157·5 kg./mm.²). The fatigue properties of the lower-strength steel were studied also in relation to the effects of surface rolling.

The fatigue strengths of the plated steels (determined by rotating-bend tests) were found to increase with increase in the intensity of the surface treatment, until ultimately they attained the values associated with unplated steels. The degree of peening required to restore the fatigue limit was approximately 0·012 A2 in the case of the lower-strength steel and 0·015 A2 for the stronger.

On the basis of data derived from investigation of the other variables considered, it is concluded that chromium plating and grinding (or grinding and chromium plating) have no significant influence on the fatigue strength of shot-peened high-strength steels and that such steels can, if necessary, be baked after plating without deleterious effects. Supplementary tests on the En25 steel, using an axial-loading (push-pull) machine to apply a variable compressive mean stress directly instead of by shot-peening, confirmed the beneficial effects of internal compressive stresses (i.e., in raising the fatigue limit of the chromium-plated steel to the 'unplated' value). The data thus obtained have enabled development of a theory which is advanced in explanation of the mechanism of failure of shot-peened and chromium-plated steel.

Pre-Heating of Steels Preparatory to Welding

'A Guide to Preheat.'
Welding Engineer, 1960, vol. 45, Feb., pp. 34–7.

The practice of pre-heating steels preparatory to welding offers three main advantages: (1) due to metallurgical changes, it promotes the formation of a tougher, more ductile weld; (2) it promotes the diffusion of hydrogen out of the weld zone, and minimizes underbead cracking and embrittlement; (3) it reduces the residual stresses in the region of the weld. The present article outlines the circumstances in which use of pre-heat is advisable, discusses the metallurgical and welding difficulties which may be overcome or minimized by use of pre-heat, describes various methods of pre-heating and indicates briefly the advantages and disadvantages of each.

The article includes a table listing suggested temperature ranges within which the following types of steel should be pre-heated: low-, medium- and high-carbon steels; low-alloy manganese steels; low-alloy molybdenum, chromium-molybdenum and nickel-molybdenum steels; low-alloy chromium steels; low-alloy high-tensile steels; and martensitic stainless steels.

Determination of Lead in Iron and Steel

BRIT. IRON AND STEEL RESEARCH ASSOC., METHODS OF ANALYSIS COMMITTEE: 'Gravimetric Determination of Lead in Iron and Steel (Lead Content > 0·05%).'
Jnl. Iron and Steel Inst., 1959, vol. 193, Dec., pp. 350–3.

In 1952 the B.I.S.R.A. Methods and Analysis Committee was asked to reconsider the analytical method laid down by *B.S.* 1121: *Part* 1*C*: 1943 for determination of lead in steels, particularly in leaded steels containing 0·2–0·3 per cent. of the metal. (The method was known to be unsuitable for materials other than carbon steels, and its accuracy was doubtful at levels below 0·1 per cent.) The procedure finally developed (full details of which are given in this paper) is based on the precipitation of lead as sulphide and conversion to lead molybdate. Recommended for determination of lead (at levels greater than 0·05 per cent.) in steel, the technique has been shown to be free from interference from chromium, copper, molybdenum, nickel, tin (up to 0·25 per cent.), and tungsten (up to 2 per cent.).

Typical results derived from analyses of a range of steels are presented. At 0·2 per cent. lead the technique is claimed to have a reproducibility of ±0·01 per cent. The method is not considered

suitable for determination of less than 0·05 per cent. of lead, and a photometric procedure is being investigated to cover these smaller contents.

HEAT- AND CORROSION-RESISTING MATERIALS

Thermal-Fatigue Cracking of Nickel-base Alloy Turbine Blades

R. A. SIGNORELLI, J. R. JOHNSTON and J. W. WEETON: 'Thermal-Stress Fatigue Cracking of Turbine Buckets Operated at 1700°F. in a Turbojet Engine with Frequent Starts and Stops.'

Nat. Aeronautics and Space Administration, Tech. Note D-125, Oct. 1959; 16 pp.

Improvements in the efficiency of gas-turbine engines have led to the development of turbine-blading alloys with satisfactory properties at the higher operating temperatures which such improvements involve. Previous investigations have, however, shown that an accurate prediction of the life or mode of failure of a given turbine-blading alloy cannot be obtained on the basis of laboratory tests alone. Moreover the principal mode of failure will vary with the engine iu which the blading is used: in the J 47 engine, in which the turbine blades operate at 1500°F. (815°C.) and are subjected to a relatively low centrifugal stress, failure occurred primarily by thermal-stress fatigue cracking at the leading edge (see abstracts in *Nickel Bulletin*, 1959, vol. 32, No. 8, pp. 261-2; No. 9-10, p. 297). Stress-rupture data on the nickel-base alloys studied in the investigations reported (see table on p. 85) indicate that they would give a possible life of 100 hours or more when used for turbine blades operating at temperatures as high as 1800°F. (980°C.). The aim of the investigations was twofold: (1) to determine the effect of engine operation at 1700°F. (925°C.) on the resistance to thermal fatigue of turbine blades in the five grades of alloy evaluated; (2) to study the mode of failure, and the rate of propagation of the cracks.

The J 47 engine employed in the tests was operated using the normal cycle of 15 minutes at rated speed and 5 minutes at idle speed. Because of the mechanical difficulties occasioned by the high test temperature, however, the engine was frequently shut down for repair work, but the frequency of starts, though high compared with that associated with similar tests run previously at 1500°F. (815°C.), was no greater than that to which a military fighter-engine might be subjected.

The primary mode of failure was found to be thermal fatigue cracking at the leading edge of the blades, and from 60 to 90 per cent. of the blades in each alloy group had developed cracks by the time the engine test was discontinued (after 70 hours and 49 starts). Some of the 'SEL-1', 'Inconel 713' and cast 'Udimet 500' blades cracked after 10-12 starts and 6½-10 hours at rated speed, while blades fabricated from the two remaining alloys cracked only after 28 starts and 30 hours' operation.

None of the thermal-stress fatigue cracks was found to progress rapidly by stress rupture, and the one blade that did fracture during the test had been operated with cracks for 31 hours (this blade fractured by progression, due to mechanical fatigue, of a crack initiated by thermal fatigue). Other blades ran with cracks for as long as 63 hours without fracture.

Nickel-base Vacuum-Melted Experimental High-Temperature Alloys

J. H. GITTUS: 'Nickel-based, Vacuum-Melted, Experimental High-Temperature Alloys.'

Metal Treatment, 1960, vol. 27, Jan., pp. 15-18.

Since the advent, in 1940, of the 'Nimonic' nickel-chromium-base creep-resisting alloys, compositional modifications and improvements in manufacturing techniques have resulted in the gradual development of a series of age-hardenable alloys, each with properties in some way superior to its predecessors. The initial alloys were produced by air-melting techniques, but use has now been made of the advantages offered by vacuum melting to produce alloys which surpass those previously available. In this paper the author outlines some of the results obtained in tests on five experimental vacuum-melted alloys which are at present the subject of patent applications: three wrought materials (designated 'M14V'*, 'M15V'* and 'M17V') and two casting alloys ('M4VC' and 'M6VC').

A note on the general characteristics of the 'Nimonic' alloys leads to a résumé of the development and properties of 'M14V', which is potentially an additional member (as 'Nimonic 110') of the 'Nimonic' series: data on tensile strength, stress-rupture characteristics, fatigue strength and high-temperature corrosion-resistance are presented. The characteristics of the remaining alloys are only briefly summarized. 'M15V' and 'M17V' exhibit even higher creep-resistance than 'M14V', an improvement which is ascribed, in part, to the formation of a larger amount of $Ni_3(Ti,Al)$-type precipitate in the matrix. Below are listed the approximate temperatures at which 'Nimonic 105' and the three vacuum-melted alloys will sustain a load of 7 tons/sq. in. (15,700 p.s.i.; 11 kg./mm.²) for over 30 hours before rupture:

'Nimonic 105'	950°C.
'M14V'	980°C.
'M15V'	1010°C.
'M17V'	1040°C.

Of the two casting materials, 'M6VC', which possesses similar stress-rupture properties to those

* Since the paper was written pilot production of 'M14V' and 'M15V' has been successfully undertaken by Henry Wiggin & Company, and the alloys have been provisionally designated 'EPK 10' and 'EPK 13', respectively.

Turbine-Blading Alloys Used in Test Programme

(*See abstract on p.* 84)

Alloy	Method of Fabrication	Composition								
		Ni %	Co %	Cr %	Mo %	Ti %	Al %	C %	B %	Nb %
'SEL-1'	Vacuum-cast	Bal. (49)	27	15	2·5	2·25	3·75	0·1	—	—
'B and B'	Vacuum-cast	Bal. (44)	30	15	5	2·5	3	—	0·5	—
'Inconel 713'	Argon-cast	Bal. (76)	—	12	4	·5	5·5	—	—	2
'Udimet 500'	Vacuum-cast	Bal. (55)	15	20	4	3·0	2·75	·1	—	—
'Udimet 500'	Wrought									

of 'M17V', is one of the most creep-resistant of nickel-base casting alloys. The 100-hour rupture stresses for 'M4VC' are higher than those for 'Nimocast 258' and the properties are reproducible to a much higher degree.

'Nimonic 90' as a Material for Springs

HENRY WIGGIN AND CO., LTD.: ' 'Nimonic 90' Heat-Resisting Alloy Springs.'
Publn. 1991*, 1960: 4 pp.

The use of higher operating temperatures in electrical appliances, industrial turbines, oil refineries, and power plant, as well as in the aircraft industry, has revealed the need for spring materials suitable for use in components (such as garter springs and circlips, relief valves, and gland springs) which are subjected in service to temperatures up to 550°C., and, in some cases, as high as 600°C. 'Nimonic 90', long established as a heat-resisting alloy in gas-turbine construction, maintains its useful spring properties for prolonged periods at temperatures up to 550°C., and for short periods up to 600°C. It is also widely used in applications requiring high resistance to corrosion-fatigue at temperatures up to 350°C.

This publication incorporates the latest data available on the physical, relaxation and mechanical characteristics of 'Nimonic 90' at temperatures in the range 20°-600°C. These data are supplemented by information on the forms in which the alloy is available and on recommended manufacturing procedures and heat-treatment.

Use of Austenitic Steels in Steam Power Plant

R. J. FABIAN: 'Materials for 1200°F./5000 p.s.i.'
Materials in Design Engineering, 1959, vol. 50, Dec., pp. 87-92.

Attempts to raise the efficiency and lower the operating costs of steam power plant have been reflected in a steady increase in operating temperatures and pressures. With each increase, the engineer has inevitably been confronted with the problem of selecting suitably heat-resistant materials of construction whose initial cost would not, in the long run, outweigh the economic advantages of the higher efficiencies resulting from their use. The new 325,000-kw. Eddystone No. 1 Power Plant, now undergoing initial testing by the Philadelphia Electric Company, is designed to operate at a pressure and temperature (5000 p.s.i. and 1200°F.: 3·5 kg./mm.^{2} and 650°C.) which are the highest yet used in a steam power plant. The conventional ferritic steels were considered unsuitable for use under these conditions, and the degree to which the austenitic stainless steels have found application in the Eddystone Plant marks a significant departure from previous practice: austenitic steels had, of course, been employed in many previous power plants, but never in such large quantities and under such severe conditions. In this article the author reviews the factors which governed the selection of materials of construction for the critical components of the plant, outlines the steels which were selected as satisfying the requirements, and reviews the problems involved in their use.

Reference is made below (under the heads employed by the author) to the steels discussed in the article.

Superpressure Turbine Materials

The turbine section of the plant is divided into several units: superpressure, very-high-pressure, high-pressure, intermediate-pressure, and low-pressure turbines. Steam at 5000 p.s.i. and 1200°F. is handled only by the superpressure turbine: the other turbines, operating under conventional conditions, make use of conventional materials. The *rotor of the superpressure turbine* (3000-lb. in weight) was forged from a 15,500-lb. ingot of Discaloy*, the material which was selected as best meeting the requirements of: adequate strength at room temperature; satisfactory

* *We shall be pleased to supply a free copy of this publication.*

* Nominal composition: nickel 26, chromium 13, molybdenum 3, titanium 1·8, per cent., remainder iron.

strength and stability at 1200°F.; optimum thermal-expansion characteristics; availability; and manufacturing and service experience. Mention is made of forging procedures and of the tests made, during forging, to ensure that the rotor would be dimensionally stable at operating temperatures and speeds. Three alternative rotors (two, of integral-disc type, in Type 422 stainless steel and in the nickel-chromium-cobalt steel 'G-18B'; the other, of separate-disc type, in 'Discaloy') were also fabricated as a precautionary measure in case of failure in the main 'Discaloy' rotor.

The first four rows of the *turbine blading* are machined from 'K-42B'†; the last two rows are in Type 422 chromium stainless steel. Although 'K-42B' has been used at 1200°F. in the form of gas-turbine blading, the alloy has never previously been used in steam turbines at temperatures higher than 1075°F. (580°C.).

The two *inner turbine casings*, weighing approximately 8,550 lb. each, were cast from Type 316 18-8-Mo stainless steel, in which the chromium and molybdenum contents were lowered, and the nickel content highered, to improve resistance to embrittlement.

The Type 316 stainless-steel main piping was welded to the chromium-molybdenum-vanadium steel outer casing by means of transition sections.

Steam-Generator Materials.

Tubing in the finishing superheater was fabricated from a heat-resisting steel containing chromium 17, nickel 14, copper 3, molybdenum 3, per cent., whose suitability for use in the range of 1250°-1350°F. (675°-730°C.) was demonstrated by comprehensive tests to determine its high-temperature and fabrication characteristics. Conventional Type 316 steel had proved unsuitable for this purpose due to the impracticable wall thickness necessitated by the service conditions.

Conventional types of stainless steel were used for the upper half of the two boilers: 18-8-Mo (Type 316) for the higher-temperature, and 18-8-Ti (Type 321) for the lower-temperature regions.

In view of the high temperatures and pressure to which they were to be exposed (the valves are designed to shut off steam between the boiler and the turbine or to permit steam to by-pass the turbine), the *valve-bodies* were fabricated from 'G-18B' heat-resisting steel.

Main-Piping Materials

Of the many materials initially considered for the main steam piping (which leads from the finishing superheater of the boiler to the turbine inlet) five were subjected to intensive study: Type 316 18-8-Mo steel, Type 347 18-8-Nb steel, a chromium-nickel-copper-molybdenum material similar to that used in the finishing superheater, '15-15N', and 'G-18B' steel. Type 316 steel was finally selected for use in the 2400 ft. of main piping used in the plant. The piping is divided into 56 fabricated assemblies, up to 50 ft. long and weighing in the region of 4-5 tons each. Since austenitic-steel piping had never before been used at 1200°F. in such large quantities, close control was required during forging, heating and bending the pipe: notes on manufacturing and welding procedures, and on the accelerated life tests to be run concurrently with the operation of the plant, are included in the article.

† Nominal composition: nickel 42, cobalt 22, chromium 18, titanium 2, per cent., remainder iron.

Fuel-Oil-Ash Corrosion of Nickel-containing Heat-Resisting Alloys

H. LEWIS: 'Corrosion by Vanadium-Pentoxide Sodium-Sulphate Mixtures in Laboratory Tests: Correlation with Corrosion by Oil Ash in Field Tests.'

Brit. Petroleum Equipment News, 1959/1960, vol. 7, Winter, pp. 48-55.

In a series of co-operative field tests, recently carried out under the aegis of the Corrosion I Committee of the Council of British Manufacturers of Petroleum Equipment, a study was made of the corrosion, by vanadium-pentoxide-bearing oil ash, of heat-resisting alloys exposed, under service conditions, in oil-fired boilers.* Laboratory tests now described covered study of the corrosion of the same heat-resisting materials, in media comprising either mixtures of the chemicals which appeared from the field tests to be the more harmful constituents of oil ash, or a synthetic oil ash previously used in research on corrosion by vanadium pentoxide. The laboratory tests were carried out in the hope that simulation of the effects observed on materials for which field-test results were already available would confirm the validity of certain laboratory techniques, and hence indicate their reliability as test criteria. Investigations under controlled conditions would serve also to confirm, or modify, the conclusions drawn from the field tests with regard to the apparent significance of certain factors in influencing corrosion. On the basis of the field-test results, it could, for example, be concluded that the relation between alloy composition and corrosion-resistance was influenced primarily by the relative proportions of vanadium pentoxide and sodium sulphate in the ash deposits. The possibility remained, however, that this apparent effect might be due to simultaneous variations in other ash constituents which would be less readily detected. Laboratory corrosion tests (employing synthetic mixtures of vanadium pentoxide and sodium sulphate as the corroding medium) offered a means of proving the ability of these substances, *per se*, to produce the effect observed in the field tests.

The resistance of the specimens was evaluated by two techniques:

(1) Weighed and emery-papered cylinder specimens were half-immersed horizontally in a synthetic oil-ash, of the following composition, for 6 hours

* For abstract of Part 1 of the report see Nickel Bulletin, 1960, vol. 33, No. 1-2, pp. 23-4.

Both Parts I and II are now available under one cover, in the form of a reprint published by The Council of British Manufacturers of Petroleum Equipment, price 5/-

at 650°, 750° or 800°C.: V_2O_5 26·5, NiO 3·0, $NiSO_4$ 6·5, Fe_2O_3 4·0, Na_2SO_4 37·0, $CaSO_4$ 12·5, SiO_2 10·5, per cent. In further tests at 750°C. the synthetic ash was replaced by 90/10 mixtures of sodium sulphate and chloride, or calcium sulphate and chloride.

A few additional steels of straight-chromium (25 and 30 per cent.) and 25-20 or 18-8 chromium-nickel type were included in the tests made by this method. The compositions of the other materials are listed in the abstract of Part 1 of the investigation.

(2) Fifty milligrams of commercially-pure vanadium pentoxide, or Analar-quality sodium sulphate, or a mixture of these two substances containing 20, 40, 60 or 80 per cent. of vanadium pentoxide, were placed in small heaps on the centre of weighed and emery-papered plates of the materials studied, and the specimens were heated in static air at 750° or 850°C. for 24 hours. In further tests (of 21 hours' duration at 850°C.) hourly additions were made of 50 mg. of the two mixtures containing 20 and 80 per cent. vanadium pentoxide.

Tests were also conducted at 850°C., using a mixture containing 79 per cent. Na_2SO_4, 20 per cent. V_2O_5, and 1 per cent. NaCl, in which both single and hourly additions were made. In the case of one nickel-base alloy, additions were made hourly, at 850°C., using mixtures containing 15 and 17·5 per cent. V_2O_5, remainder Na_2SO_4.

The corroded cylinders and plates were descaled electrolytically in molten caustic soda, washed, dried, and finally re-weighed to determine loss in weight. Duplicate samples, exposed to the same treatment but not descaled, were subjected to metallographic examination.

Full details are given of the data obtained by means of each of these two procedures. Discussion of the corrosion behaviour observed is supplemented by photomicrographs of corroded specimens.

The author's summary of the main conclusions is quoted below:

'(1) Accelerated oxidation of a series of heat-resisting alloys, with varying degrees of sulphur penetration (similar to that observed in specimens of the same alloys exposed to ash corrosion during field tests in oil-fired boilers) can be reproduced in tests in air at 850°C. by repeated deposition on the specimens, at hourly intervals, of V_2O_5/Na_2SO_4 mixtures. With a mixture containing 20 per cent. vanadium pentoxide, the order of merit of the alloys is approximately the same as in field tests under oil-combustion conditions which give rise to deposits of high Na:V ratio: when the mixture contains 80 per cent. vanadium pentoxide, the order of merit is approximately the same as observed under oil-combustion conditions in which ash deposits of low Na:V ratio are formed.

'(2) Partial-immersion tests, in a synthetic mixture of intermediate Na:V ratio regarded as typical of the composition of oil ash, also reproduced the general features of the attack suffered in field tests, but gave an order of merit slightly different from that in a field test in which the ash deposit had a similar Na:V ratio: the behaviour in this case resembled more nearly that observed in a field test in which the Na:V ratio was higher.

'(3) Sulphur attack by vanadium-pentoxide/sodium-sulphate mixtures is accelerated by the addition of sodium chloride to the mixture, and corrosion by sodium-sulphate/sodium-chloride mixtures is similar to that resulting from vanadium-containing oil ash of high sodium-sulphate content. The presence of chlorides does not, however, appear essential to promotion of the types of corrosion produced in oil-fired boilers.

'(4) In 24-hour oxidation tests, with prior contamination of the specimens by a single small deposition of vanadium-pentoxide/sodium-sulphate mixtures, the most severe attack was caused by mixtures containing 20 to 40 per cent. sodium sulphate. The most susceptible alloys were those of highest iron and lowest nickel contents. The nature of the attack is similar to that produced by pure vanadium pentoxide, though it is, in some cases, more severe. Such a method of test fails to reproduce the sulphur contamination which results in severe attack of high-nickel alloys exposed to continuous deposition of oil ash of high sodium-sulphate content.'

Study of Hexagonal Carbide and Nitride Phases Present in Steels

See abstract on p. 82.

Abnormal Grain Growth in Austenitic Steels

B. CINA: 'Abnormal Grain Growth in Austenitic Alloys.'

Jnl. Iron and Steel Inst., 1960, vol. 194, Jan., pp. 18-28.

Experience with certain creep-resistant stable austenitic alloys of high-work-hardening type has shown that abnormally large grains are sometimes developed in forgings or in hot-rolled bar after final solution or softening treatment at elevated temperatures. Since these abnormal grains may have an adverse effect on the tensile and fatigue properties of the material, and may also affect the creep properties, the work described was undertaken to establish the conditions governing their formation, to study the mechanism involved, and to determine some means of avoiding abnormal grain growth. The prior history and the initial grain-size of the steel are influential factors and, as such, were considered during the investigation.

The composition of the three steels selected for study are given in the table on page 89. All three steels were supplied in the form of hot-rolled bar heat-treated to achieve a uniformly fine-grained condition.

The samples were forged (under laboratory conditions) at 800°, 900°, 1000°, 1100° or 1150°C., to achieve deformations ranging from 0-128 per cent. To determine the extent of grain growth after controlled amounts of hot deformation, 'NMC' specimens were held, for times up to 9 hours, at 1120°C.

(the forging temperature) or 1050°C. (the softening temperature). In the case of 'FV 337' and 'FV 467', a study was made of the influence of holding hot-deformed samples for periods of ¼ hour at, respectively, 1225° and 1235°C. (the solution-treatment temperatures conducive to abnormal grain growth), and the effects of varying the rate of heating to, and the time of holding at, the solution-temperature were also investigated. Complementary to the laboratory tests, rolling trials were carried out on 'FV 467' bar material.

The data obtained are discussed in relation to the mechanism of grain growth and methods of minimizing abnormal grain growth. The salient findings of the study are summarized as follows:

'(1) Abnormally large grains (greater than A.S.T.M. 0) have been found to develop on solution or softening treatment of certain fully austenitic alloys.

'(2) The formation of these grains is associated with the prior hot-working history of the material, but can also be brought about, in initially fine-grained recrystallized samples, after critical amounts of deformation at controlled temperatures followed by solution-treatment.

'(3) These grains are believed to form by a mechanism of secondary recrystallization, and evidence has been obtained for the development of deformation textures during hot working, and subsequent recrystallization textures, which would provide the necessary conditions for such a mechanism.

'(4) The rate of grain growth has been found to be in part dependent on the solution of a sufficient number of fine carbide particles, whose presence otherwise impedes grain growth.

'(5) The effect of initial grain-size was such that secondary recrystallization could be induced only in initially fine-grained material. Hot deformation of initially coarse-grained material resulted only in grain refinement on subsequent treatment at elevated temperatures.

'(6) Simple methods have been found to minimize abnormal grain formation. In two of the alloys, the method consists of subjecting fine-grained recrystallized material to a small uniform amount of deformation, at a particular temperature, just before the final solution or softening treatment. For the third alloy ('NMC'), a deformation in excess of the critical had to be applied.'

Metallographic and Corrosion Studies of Stainless Steel Using Potentiostat Techniques

V. ČÍHAL and M. PRAŽÁK: 'Corrosion and Metallographic Study of Stainless Steels Using Potentiostat Techniques.'

Jnl. Iron and Steel Inst., 1959, vol. 193, Dec., pp. 360–7.

Electrochemical studies of stainless steels can be carried out by measuring corrosion rates either at constant current or at constant potential of the working electrode. The use of the electronic potentiostat to maintain a constant potential, and the advantages offered by this technique in investigation of the corrosion behaviour of stainless steels, are discussed in the introductory section of the paper. An outline is given of the characteristics of the particular potentiostat employed to determine the polarization curves which, later in the paper, are used to illustrate these advantages, and the significance of the polarization curve is discussed in relation to the light it throws on the corrosion behaviour of 18-8 steel in 5 per cent. sulphuric acid.

In the main section of the paper a brief discussion of intercrystalline corrosion of stainless steels is introduced by examination of polarization curves indicating the effects of chromium, nickel and other alloying elements on the corrosion current of stainless steels in regions of activity, transpassivity and secondary passivity. It is then pointed out that since, in a steel containing two or more phases, each phase has a certain characteristic polarization curve, comparison of these curves enables selection of a potential at which a particular phase will be preferentially attacked. By electrolytic etching of stainless steels under controlled-potential conditions, it is thus possible to differentiate and identify phases of different chromium content (sigma, delta ferrite, austenite): etching conditions for 18-8 stainless steels are tabulated. The paper ends with brief notes on the use made of this type of etching technique to study transformation of delta ferrite in 18-9-Ti steel.

Use of the Potentiostat to Study Intercrystalline Corrosion of Stainless Steel

L. CLERBOIS, F. CLERBOIS and J. MASSART: 'Intercrystalline Corrosion of Austenitic Stainless Steels.'

Electrochimica Acta, 1959, Apr., pp. 70–81; disc., pp. 81–2.

The paper was written with a dual aim: (1) to present the findings of a study of the corrosion behaviour of austenitic stainless steels; and (2) to give details of a test proposed as a means of evaluating the susceptibility of such steels to intercrystalline corrosion.

In phase one of the test programme a study was made of the modes of corrosion of the following five grades of chromium-nickel austenitic stainless steel, using a potensiostat technique (previously employed by Edeleanu and Carius) to determine polarization curves of specimens immersed in $2N$ H_2SO_4 at 20°C.: 18-8, low-carbon 18-8, 18-8Mo, 18-8Ti and 18-8Nb (i.e., Types 302, 304LC, 316, 321, 347). Prior to testing, each of the steels was subjected to a sensitizing heat-treatment at 650°C.

The polarization curves presented are characterized by features associated with the specific aspects of corrosion behaviour which are noted below:

(1) *General corrosion* was observed at an electrode voltage in the range −400 to −100 mV. (although the behaviour of the various steels studied differed considerably in this respect).

Composition of Austenitic Steels

(*See abstract on p. 87*)

Steel	Composition										
	C %	Si %	Mn %	S %	P %	Cr %	Ni %	Co %	Mo %	Cu %	Ti %
'NMC'	0·63	0·41	7·45	0·008	0·034	4·00	8·35	—	—	—	—
'FV 337'	0·20	0·74	0·69	0·012	0·025	17·52	17·68	6·83	2·66	2·73	0·74
'FV 467'	0·22	0·62	1·11	0·003	0·015	13·8	9·55	—	2·18	2·5	0·78

(2) When the steel was sensitized and unstabilized, and the carbon content was sufficiently high, *intercrystalline corrosion* occurred at voltages in the range −100 to 0 mV.

(3) *Passivity* occurred at a voltage between 0 and 750 mV.

(4) At voltages higher than about 750 mV, the steel was subject to severe corrosion, which occurred mainly in the form of a thick band around the grain boundaries, but, in some cases, extended to the entire surface of the grains. This type of attack, the result of dissolution of chromium in the hexavalent state, increases in intensity with increase in the oxidizing character of the solution and in the chromium content of the steel.

The second part of the paper is concerned with an electrochemical study of two widely accepted tests for determining susceptibility to intergranular corrosion: the Strauss and Huey tests. The authors indicate the imperfections of each technique and discuss the reasons for the divergences observed in the results obtained. They come to the conclusion that, provided certain precautions are taken (e.g., adding metallic copper to the solution and preventing impoverishment of the reagent), the Strauss test is specific in so far as intercrystalline corrosion is concerned. The Huey test, on the other hand, is considered valid only when used to assess corrosion-resistance in a strongly oxidizing medium, and is in no way suitable for determining resistance to intercrystalline corrosion: it is pointed out, for example, that a low-carbon molybdenum-containing steel which would be severely corroded in the Huey reagent can be used perfectly reliably without recourse to heat-treatment. The potensiostat technique is considered a more rational test than the empirical tests based on the Strauss or Huey procedures, and its use as an acceptance test for stainless steels is therefore urged. In evaluating intercrystalline corrosion-resistance, use of the following test conditions is recommended:

Electrolyte: 2*N* H_2SO_4
Temperature: 20°C.
Electrode voltages: −100 mV
Duration of test: 24 hours.

A bend test after exposure is deemed a sufficient qualitative criterion of resistance.

Corrosion-Resistance of Stainless Steels, Nickel and High-Nickel Alloys in Marine Environments

J. C. ROWLANDS: 'Stainless Steels and Related Alloys Versus Marine Evironments.'
Corrosion Technology, 1959, vol. 6, Dec., pp. 359–63.

The test programme reported was undertaken in view of the envisaged use, in naval applications, of stainless steels for under-water fittings. Although the literature contained much information on the corrosion behaviour of specific types of stainless steel in sea-water, the differences in test conditions precluded any attempt at a comparative assessment of the merits of the different grades studied. The aim of the present investigation was to obtain a quantitative evaluation of the relative corrosion-resistance, in sea-water, of representative corrosion-resisting steels and alloys.

Four grades of material were tested (all in the annealed condition):

(1) *Chromium-(nickel) martensitic stainless steels* of the following type: 12-0; 12-0-Al; 12-0-Mo; 14-0; 14-0-C; 13-0-HC; and 17-2-C.

(2) 17 *per cent. chromium ferritic stainless steel.*

(3) *Chromium-nickel austenitic stainless steels* of the following type: 18-8; 18-8-Ti; 18-8-Mo; 18-8-Mo-Ti; 18-10; 18-10-Nb; 18-18-Mo-Ti-Cu; 25-22; and 10-37-HC.

(4) *High-nickel alloys* of the following type: 65 Ni-15 Cr-20 Fe; 80 Ni-15 Cr-5 Fe; 70Ni-29 Cu-1 Fe; nickel.

Carbon contents between 0·15 and 0·25 per cent. are indicated by the symbol 'C' and higher values by 'HC'; lower contents are not indicated.

Sheet specimens of these materials were:

(1) Fully immersed in sea-water (in Chichester harbour) for periods of 3–20 months in the following conditions: after deposition of a weld bead; in the

as-received condition; electropolished; fine-polished; coarse-polished; shot-blasted; and (in the case of the 17-2-C material) hard-chromium-plated.

(2) Subjected, in the as-received bright condition, to half-tide and to aerial exposure for periods of up to 9 years.

(3) Subjected during complete immersion, to galvanic-corrosion tests by coupling them with copper or with mild steel.

(4) Subjected, again under complete-immersion conditions, to crevice-corrosion tests of up to 30 months.

The corrosion rates determined are presented in the paper in terms of weight-loss per unit area per day.

Visual examination of the total-immersion specimens revealed that the stainless steels corroded mainly as a result of crevice attack due to marine fouling, and the corrosion rates given are, therefore, a measure of the tendency towards fouling and of the extent of the subsequent crevice attack. In general, the austenitic steels exhibited the highest corrosion-resistance, while the martensitic steels were found to be more resistant than the high-nickel alloys (which appeared to have poor resistance, only slightly better than that of the ferritic steels). The failure of chromium plating to protect the 17-2-C steel is ascribed to the porosity of the chromium deposit, and it is considered possible that corrosion-resistance would have been increased by deposition of a copper or nickel undercoat prior to chromium plating.

Crevice corrosion, although still the major type of attack, was much less severe under half-tide conditions than under full-immersion conditions, an effect which was probably due to the re-annealing of the surface film when the specimens were dry. No evidence of significant attack was found on samples exposed under aerial conditions, but all the steels exhibited a tendency to rust, and the surfaces of all the specimens were tarnished.

The results of the galvanic-corrosion tests appeared to be related to data listed on the potential exhibited by the materials in sea-water.

None of the specimens tested was found to be immune to crevice corrosion, but, on the basis of the tests carried out under crevice conditions, the four grades of material are placed in the following descending order of resistance: austenitic steels; high-nickel alloys; ferritic steels; martensitic steels. The 18-8-Mo steel appeared least susceptible to crevice corrosion. Extreme care should be taken to prevent onset of this type of attack, since severe localized corrosion is far more dangerous than a general overall attack. A certain degree of protection against crevice corrosion may be conferred by the use of chromate jointing compounds, but this procedure is not always practicable.

The paper ends with notes on a technique in which accelerated crevice attack on stainless-steel bar specimens is induced by local electrolytic depassivation of a small area, followed by rapid formation of a crevice around the activated area (using a tight polythene sleeve for the purpose).

Penetration of Alloys by Liquid Metals and Salt Melts

J. D. HARRISON and G. WAGNER: 'The Attack of Solid Alloys by Liquid Metals and Salt Melts.'
Acta Metallurgica, 1959, vol. 7, Nov., pp. 722-35.

In the introductory section of the paper the authors show that if one component of a solid alloy is preferentially leached out by a liquid metal or a salt melt at elevated temperatures, then a plane solid/liquid interface is not stable and, hence, a highly-rugged interface might develop. The work reported was carried out to gain confirmatory evidence in this respect, and to study the factors involved in the phenomenon.

In accordance with the findings of the theoretical analysis a rapidly-advancing liquid penetration was determined:

(1) in solid copper-nickel alloys (copper 18-87 at. per cent.) immersed in liquid silver at 1000°C., i.e., under conditions involving preferential dissolution of the copper;

(2) in solid gold-copper alloys (gold 61 and 74 at. per cent.) immersed in liquid bismuth at 400°C., i.e., under conditions involving preferential dissolution of the gold; and

(3) in specimens of a solid silver-gold alloy (gold 12 at. per cent.) from which silver was dissolved anodically in molten AgCl at 800°C.

In contrast to these results, data gained from a study of copper-nickel alloys in liquid bismuth at 800°C. demonstrated that where, as here, the solubilities, in the solvent, of the two constituents of the alloy are similar, there is no pronounced tendency towards preferential leaching, no instability of a plane solid/liquid interface, and hence no occurrence of ruggedness at the interface.

Corrosion of Stainless-Steel Tubes in a Hydrogen-Reforming Furnace

K. L. MOORE: 'Corrosion of Furnace Tubes by Residual Welding Slag.'
Corrosion, 1960, vol. 16, Jan., pp. 26t-8t.

The corrosion failures which form the subject of the paper occurred in the tubes of a hydrogen-reforming furnace of a hydrogen plant constructed by the Tidewater Oil Company at its Delaware refinery. The furnaces are designed to operate at pressures of 120-150 p.s.i., and the tubes (packed with nickel reforming catalyst, which converts the hydrocarbon and steam into hydrogen, carbon dioxide and carbon monoxide) operate at a skin temperature of 1600°-1700°F. (870°-925°C.) and at outlet-reaction-gas temperatures of 1450°-1500°F. (785°-815°C.).

The tubes were fabricated by welding together two 15-ft. (4·5 m.) lengths of 5-in.- (12·5-cm.-) diameter extruded tubing in 34-21 nickel-chromium-iron alloy. The circumferential weld, produced using a 68-15 nickel-chromium-iron welding rod,

was located in the centre of the firebox. The root pass was made under inert gas, and subsequent passes were effected with a coated electrode. The welds were wire-brushed after completion.

Inspection of the plant revealed that, after only three weeks' service, deposits had developed on some of the tubes in the region of the weld. On the basis of subsequent investigations, this type of catastrophic attack was ascribed to the conjoint effects of the presence of residual welding slag, sulphur and of reducing conditions, and for satisfactory service it is considered essential to avoid high-sulphur and reducing conditions (even in the absence of residual welding slag).

Immunity from high-temperature corrosion by welding slag can be conferred by (1) thoroughly sandblasting welds and splattered areas, or (2) welding with a bare wire, under inert gas, to avoid introduction of flux, or (3) ensuring, by testing under operating conditions, that any slag formed is innocuous.

It is emphasized that wire-brushing, or even grinding, is not an adequate precautionary measure if the operation temperatures are in the corrosive range (which can be as low as 1200°–1300°F. (650°–705°C.)).

Prevention of Sulphide Stress Cracking in Sour-Condensate Well Equipment

W. J. McGUIRE and L. W. VOLLMER: 'Prevention of Sulfide-Stress Cracking in Sour-Condensate Well Equipment.'

Amer. Soc. Mechanical Engineers, 1959, *Paper* 59-PET-36; 11 pp.

The failure of steels exposed under stress to hydrogen-sulphide environments (conditions which obtain in the production of sour heavy crude oil from deep high-pressure condensate wells) has been the subject of intensive research since the first failures occurred in critical items of oil-well equipment. The factors believed to contribute to the occurrence of sulphide stress cracking, and theories advanced to explain its mechanism, are outlined in the introductory section of this paper. The main aim of the author is, however, to present case-histories of spontaneous brittle failures (encountered at Pincher Creek, Alberta, but typical of those experienced generally in sour-condensate fields), to comment upon the nature of the failures, and to indicate the means developed to prevent any recurrence.

Sub-surface equipment discussed in this connexion includes tubing and casing in 'N-80' (manganese-molybdenum) steel and tubing in 9 per cent. nickel steel and in chromium-molybdenum (A.I.S.I. 4140 and 4145) steel. Sulphide stress cracking of surface equipment, and methods of preventing the onset of such failure, are described in the light of experience with valve stems (fabricated from A.I.S.I. 4140 and 410 steels and 'K Monel') and valve bodies.

In summarizing the points raised in the paper the authors emphasize that freedom from sulphide stress cracking can be achieved by selection of suitable materials, by appropriate design, and by maintaining the applied stress at a minimum level. With respect to suitable materials they make the following recommendations:

'(1) When well conditions permit, grade 'J-55' tubing made from plain-carbon steel should be used. If the engineering requirements are such that 'J-55' is inadequate, specially processed 'N-80' is indicated. Experience has shown that the carbon-manganese-molybdenum steels and A.I.S.I. 4140 or 4145 can be rendered insensitive to sulphide stress cracking by tempering, at a minimum temperature of 1150°F. (620°C.), to develop yield strengths in the range 75,000 min. p.s.i.–90,000 max. p.s.i. (33·5–40 t.s.i.; 52·5–63·5 kg./mm.^{2}). Specially treated 'N-80' casing is not now available, and to avert sulphide-stress-cracking failures in potentially susceptible 'N-80' materials, it is necessary to exclude the well fluids from the casing-tubing annulus. This can best be accomplished by using bottom-hole packers and by insuring against leaks in the tubing joints.

'(2) Critical components of wellhead equipment that require materials with hardnesses of Rockwell C 30 or greater should be made of 'K Monel', which, under the conditions encountered in sour-condensate-well service, is immune to cracking.

'(3) Equipment that is fabricated by welding, or which may be repaired by welding, should be thermally processed after welding to limit hardness to 225 Bhn maximum.'

Selection of Materials for Refinery Processing Equipment

A. J. FREEDMAN, G. F. TISINAI and E. S. TROSCINSKI: 'Selection of Alloys for Refinery Processing Equipment.'

Corrosion, 1960, vol. 16, Jan., pp. 19t–25t; disc., p. 25t.

The introduction of new petro-chemical processes, and the increase in the severity of refinery operating conditions associated with the drive for higher-octane petrol, have re-emphasized the vital importance of selecting the most suitable materials of construction. Preconceived ideas concerning the use of particular materials under given service conditions will, in the authors' opinion, have to be discarded in favour of a carefully planned and executed evaluation programme, which 'should consider all possible variables which might influence alloy performance during construction and normal operating cycles, including both on-stream and shutdown periods'. This paper discusses the process variables which influence the selection of materials for refinery processing equipment.

In the introductory section of the paper brief case histories of failures are presented to instance and emphasize the dangers inherent in using materials of construction for new processing plant without first evaluating their suitability in relation to the

process variables. Attention is then directed to the factors which must be taken into account if corrosion testing (both in the laboratory and pilot-plant stages) is to be carried out efficiently and economically: the effects of temperature, time, stream concentration, galvanic corrosion, additives, and process modifications are given special consideration. The metallurgical features of a given alloy or steel will govern its corrosion-resistance in a specific media, and therefore also call for careful study: in this connexion, the authors comment on weld-metal structure, grain-boundary precipitation in stainless steels and alloys, stress corrosion, hydrogen attack, and problems associated with clad steels.

Finally emphasis is placed on the need to maintain effective records of the test, chemical composition and heat-treatment relevant to each specimen, and on the desirability of continuing the evaluation during plant operation, using corrosion monitoring devices installed at various locations throughout the plant. The points raised in the text are illustrated by data on 'Hastelloy C' and various grades of 18-8 stainless steel.

'Illium 98': Nickel-base Alloy Resistant to Sulphuric Acid

T. E. JOHNSON: 'New Ni Alloy Cuts Hot Sulfuric Bite.'
Chemical Engineering, 1959, vol. 66, Dec. 14, pp. 194, 196, 198.

Until recently pumps, valves and other components subjected in service to flowing sulphuric acid were seldom exposed to the acid at temperatures higher than 185°F. (85°C.). A relatively minor increase in temperature substantially decreases the corrosion-resistance of materials in sulphuric acid, and, since many process plants now operate at 230°F. (110°C.) and, in some cases, at temperatures as high as 300°F. (150°C.), the metallurgist has been confronted with the problem of developing an alloy with the corrosion-resistance requisite for such service. This article outlines the properties and advantages offered by 'Illium 98', an alloy, of the following nominal composition, evolved by Stainless Foundry and Engineering, Inc., Milwaukee, as a solution to this problem: nickel 55, chromium 28, molybdenum 8·5, copper 5·5, manganese 1·25, iron 1·0, silicon 0·7, carbon 0·05, per cent.

As shown by the corrosion data included in the article, the alloy exhibits excellent resistance to sulphuric acid over a wide range of concentrations at 80°C. Its resistance to the acid in the concentration range 60–90 per cent. is much superior to that exhibited by the complex chromium-nickel steel 'Stainless 20' and by 'Illium C', the material from which the new alloy was developed. At temperatures higher than 80°C., however, 'Illium 98' is subject to attack (a corrosion rate of 0·02 in./year (0·5 mm./year) is deemed a criterion of satisfactory resistance) in acid at concentrations of 60–90 per cent. The material should not be used in contact with wet bromine and iodine, chloracetic acid, moist chlorine gas, cupric chloride, ferric chloride or hydrochloric acid.

Stated to have good resistance also to non-halogen acids, the alloy is readily machinable and is weldable by arc-, inert-arc-, or acetylene-welding techniques. The following mechanical properties are quoted as characteristic: tensile strength 54,000 p.s.i. (24 t.s.i.; 38 kg./mm.^{2}); elongation in 2 inches, 18 per cent.; reduction in area, 22 per cent.; Brinell hardness, 152–167.

Notes on the metallurgical factors and the research involved in the development of 'Illium 98' conclude the article.

Nickel-base High-Temperature Alloys for Use in the Glass Industry

B. F. RICHARDSON: 'High-Temperature Alloys for the Glass Industry.'
Glass Industry, 1959, vol. 40, Aug., pp. 421–2, 445; Sept., pp. 473–5, 498; Oct., pp. 530–1, 560, 562.

In this paper the author summarizes the properties of the nickel-base heat-resisting alloys of the 'Viscotherm' series, and considers the advantages they offer to, and the applications they find in, the glass industry. The alloys, which contain significant percentages of chromium, cobalt and molybdenum and are rendered age-hardenable by aluminium and titanium additions, are stated to exhibit excellent hot-strength and to be widely used in the glass-manufacturing industry for components subjected in service to temperatures up to 1300°C.

Part I of the paper is concerned with the mechanical properties, the microstructural characteristics and the machinability of the 'Viscotherm' alloys (as exemplified by grades 4, 5, 6, 7, or 1612 of the series).

In Part II, the applications which the alloys find in glass-manufacturing operations are typified in terms of the particular property required during service (*viz.*, a high melting point and satisfactory hot-strength; thermal stability at high temperatures; resistance to spalling, flaking and sloughing; resistance to thermal shock; insignificant gas content). Typical applications include those associated with gathering operations (bushings, tips, pins, irons), feeding operations (orifices, plungers, shears), and forming operations (moulds, plungers, pins, mandrels).

During the development of the 'Viscotherm' alloys full account was taken of the advantages derivable from vacuum induction melting. The vacuum-melting equipment and procedures employed in the production of the alloys form the subjects of the third, and last, part of the article.

Prevention of Pitting on the Surface of Investment-Cast Stainless Steels

L. W. DUFFEN and D. C. JARMAN: 'Pitting on Investment-Cast Corrosion-Resistant Steels.'
Brit. Foundryman, 1960, vol. 53, Feb., pp. 79–82.

Since the end of World War II investment-casting techniques have been applied to many alloys and steels formerly cast by other methods. The as-cast surface finish of some of these materials has not, however, been of the standard expected and

required: a major defect has been that of surface pitting. In the investment foundry with which the authors are associated (de Havilland Engine Company, Ltd.) pitting has caused the rejection of many stainless-steel castings. This paper outlines the work which has resulted in a solution to the problem.

Six types of corrosion-resisting steel were selected for study: a 10 per cent. and a 12 per cent. chromium steel, and chromium-nickel steels of 16-5, 18-2, 18-11 and 23-12 type. (It has been proved in practice that a chromium content higher than 20 per cent. and a nickel content higher than 10 per cent. render the steel more resistant to surface pitting, and a steel of 23-12 type would therefore give no trouble at all.) The influence of two variables was investigated: the manner of firing the mould, and the silicon/manganese ratio.

A mechanism is advanced in explanation of the pitting phenomenon. Pitting is shown to occur, after solidification of the casting, by formation of a metal oxide and the subsequent reaction of the oxide with the refractory mould. It can be prevented by cooling the casting in an oxygen-free atmosphere.

Centrifugally-Cast Steel Pipe

J. T. GOW: 'Centrifugally-Cast Steel Pipe and other Tubular Products.'

Foundry Trade Jnl., 1959, vol. 107, Dec. 10, pp. 579-85.

The Sandusky Foundry and Machine Company, Ohio, engages exclusively in the production of centrifugally-cast tubes and cylinders, from 7 to 45 in. (17·5-112 cm.) in outer diameter and up to 33 ft. (10 m.) long, in a variety of materials, including heat- and corrosion-resisting stainless steels, carbon and low-alloy steels, and copper- and nickel-base alloys. In this paper the author discusses the fundamental factors involved in, and illustrates the advantages of, the centrifugal-casting process.

In the introductory section of the paper details are given of the type of casting machine and metal mould employed, and the speed of rotation of the mould and the solidification process are discussed. Account is then taken of the main factors governing the occurrence of such defects as composition gradients across the wall section, cracking or hot-tearing, circumferential lapping, and segregation banding. The influence of the spinning speed, the rate and temperature of pouring, heat-extraction from the mould, and of the radial pressure during solidification is discussed in this connexion and exemplified by data on stainless-steel castings. Data are included also on the dimensional allowances necessary to permit the machining operations requisite for the production of a clean and sound finished product.

Tensile data for castings in mild steel and straight-chromium and 19-9 chromium-nickel stainless steels are tabulated to illustrate the ability of tubular centrifugal castings to conform readily to the requirements of the various A.S.T.M. casting specifications which entail the taking of test sections from well-fed test blocks. A comparison of the yield strengths of centrifugally-cast and wrought grades of 18-8 and low-carbon 18-8 (Type 304 and 304L) austenitic steels demonstrates that the strength of the cast grades is (over a wide range of temperature) at least equal to that of the wrought in the annealed condition.

Determination of Nickel and Cobalt in Stainless Steels

See abstract on p. 70.

Pre-Heating of Steels Preparatory to Welding

See abstract on p. 83.

Notch-Rupture Strength of the Heat-Affected Zone of 18-8-Nb Weldments

R. J. CHRISTOFFEL: 'Notch - Rupture Strength of Type 347 Heat-Affected Zone.'

Amer. Soc. Mechanical Engineers, 1959, *Preprint* 59-*MET*-13; 11 pp.

A.I.S.I. Type 347 niobium-stabilized 18-8 chromium-nickel stainless steel has been used for steam-turbine components and piping systems for a number of years, in general, with satisfactory results. In some instances, however, the material has cracked during service, usually in the heat-affected zone of weldments. Research by other investigators had shown that cold working significantly increases the yield strength, rupture strength and creep strength of Type 347 steel and drastically reduces its creep-rupture ductility. Since the heat-affected zone of an austenitic weldment is hot-cold-worked over a range of temperatures during welding, it was thought feasible that, in the as-welded condition, the heat-affected zone of a Type 347 joint might exhibit poor notch-rupture strength, which, in turn, might then contribute to the cracking of the as-welded joint. The investigation now reported was conducted to determine the notch-rupture strength of the heat-affected zone of welded joints in Type 347 stainless steel.

The basis metal was obtained from a solution-treated forging, of the following composition, the dimensions of which were such as to provide adequate restraint during welding: carbon 0·06, silicon 0·64, manganese 1·5, sulphur 0·022, phosphorus 0·025, chromium 18·8, nickel 9·5, niobium 0·57, per cent. Smooth and notch-rupture bars were machined from the forging to act as control specimens. Two grooves machined in the opposite faces of the forging were then welded, using a low-ferrite Type 347 electrode, and one welded groove was slabbed off and left in the as-welded condition, while the other was subjected to a solution-treatment. Notch-rupture bars were machined, transverse to the axis of each groove, such that the notch was located in the heat-affected zone of the basis metal, approximately $\frac{1}{32}$ in. (0·8 mm.) from the fusion line. The welds were subjected to microstructural examination, and hardness measurements were also made. Rupture tests were carried out at 1100° and 1200°F. (595° and 650°C.) for times ranging from 10 to 3000 hours. The microstructures of notch specimens broken in short- and long-time tests were examined.

Supplementary to the main test programme, experiments were made (1) to distinguish the thermal effects on the heat-affected zone from those of mechanical strain, and (2) to determine whether the notch-rupture strength of the heat-affected zone (in the as-welded condition) would be influenced as significantly if a 16-8-2 chromium-nickel-molybdenum welding electrode were used instead of the Type 347. The former tests indicated that the thermal cycle had essentially no effect on the notch-rupture strength of the as-welded material; the results obtained in the latter were fundamentally the same as those obtained using Type 347 weld metal.

The data presented are discussed first in relation to the light they throw on the factors involved in cracking, and then in relation to their validity as applied to welded joints in turbine installations. The author summarizes his conclusions as follows:

'The results obtained in this investigation show, for the first time, that the heat-affected zone of the sound weld joint (i.e., not considering those cases where actual cracking is produced in the heat-affected zone because of poor hot-ductility during welding) in 347 material in the as-welded condition has properties inferior to those of the unwelded material or to the post-weld solution-treated heat-affected zone. It is likely that the low notch-rupture strength of the heat-affected zone was a contributing factor to the cracking which occurred in this region in the pipe-weld joints mentioned at the beginning of the paper. It is not considered that this is the only cause of the cracking, since the notch rupture strength would still be well above the average service stress of approximately 5000 p.s.i. However, in the presence of residual welding stresses at a high level, or bending stresses and the service stresses, the low notch-rupture strength would be the final contributing factor leading to premature failure.

'The desirability, on the basis of these results, of giving completed weld joints in Type 347 material a post-weld solution-treatment is also emphasized. It can be seen now that, in addition to solutioning and spherodizing ferrite in the weld metal and relieving the residual welding stresses, post-weld heat-treatment also improves the notch-rupture strength of the heat-affected zone. Welds in Type 347 material should therefore always be given a post-weld solution-heat-treatment for maximum assurance of satisfactory service performance.'

Study of Sigma Phase in Austenitic/Ferritic Weld Metal

N. YA. KARASIK and N. E. SHLEPYANOVA: 'Physico-Chemical Investigation of Sigma-Phase Modifications in Austenitic-Ferritic Weld Metal.'

Avtomaticheskaya Svarka, May, 1959.
Translated in *Automatic Welding*, 1959, Aug., pp. 63-71.

In the work described phase formation in stainless-steel deposits of 19-10-1Nb type was studied, using chemical and X-ray techniques, with the aim of establishing the nature and composition of the phases formed and the effect of these phases on the properties of the metal. The σ phase was the subject of particular study.

Two weld-metal compositions were selected for investigation: one was fully austenitic, the other contained about 5 per cent. of ferrite. The two types of weld metal were examined in the as-deposited, stabilized, stabilized+aged, austenitized+stabilized, and austenitized+stabilized+aged conditions.

The data obtained demonstrate that the formation of σ phase is more intensive in the presence of ferrite, and that the amount of σ phase formed during ageing influences the impact strength of the weld metal: the presence of 6-9 per cent. of σ phase reduces impact strength to a value as low as 2 kgm./cm.^{2}.

Chemical and X-ray analysis established the existence of two modifications of σ phase. In one of these the iron/chromium ratio is in the region of 1, in the other the ratio is about 2.

Use of a 20 per cent. aqueous solution of hydrochloric acid at a low current density (0·02 amp./cm.^{2}) was found a satisfactory method of extracting σ phase from the parent metal.

475°C. Embrittlement in Stainless-Steel Weld Metal

V. I. DYATLOV and N. I. KOPERSAK: 'The Nature of 475°C.-Brittleness in Chromium-Nickel Stainless Steels.'

Avtomaticheskaya Svarka, May, 1959.
Translated in *Automatic Welding*, 1959, Aug., pp. 78-98.

The embrittlement which occurs in certain chromium stainless steels after prolonged heating in the temperature range 400°-450°C. is reported to develop also in 18-8-type chromium-nickel steels of dual-phase (γ+α) microstructure. Since optimum resistance to intercrystalline corrosion and hot-cracking is associated in 18-8-steel welds with an austenitic/ferritic structure, the study of '475°C. embrittlement' is of obvious interest to the metallurgist. The present investigation was initiated to study the factors involved in the development of such embrittlement in weld metal, of the following composition, containing 65 per cent. ferrite: carbon 0·06, silicon 0·73, manganese 1·0, sulphur 0·019, phosphorus 0·021, chromium 27·8, nickel 9·7, per cent.

Embrittlement (as reflected in variations in microstructure, microhardness and impact strength after long-time exposure at 475°C.) was studied not only in relation to the un-treated weld metal, but also as a function of prior homogenization treatment, of subsequent heat-treatment at 540°, 580°, 650°, 750° and 1000°C., and of the temperature of impact testing.

Consideration of the extensive data obtained leads the authors to conclude that 475°C. embrittlement

is due to the processes, in α-iron highly-alloyed with chromium, of intra-phase redistribution of chromium with no separation of excess phases. The redistribution causes distortion of the crystal lattice and brings the ferrite phase into the 'intra-phase work-hardened' state, reflected in a sudden decrease in impact strength and increase in the microhardness of the ferrite.

A close relationship exists between 475°C. embrittlement and the formation of σ phase at higher temperatures, and the intra-phase redistribution of chromium is regarded as the incubation period for formation of σ phase. It is suggested that a more suitable name for the phenomenon would be 'σ ageing in chromium and chromium-nickel steels'.

Since σ ageing is a diffusion process, it is considered that embrittlement can develop also at the temperatures below 475°C. at which in practice chromium diffusion may occur. It is considered also that σ ageing may develop not only in ferritic and austenitic/ferritic steels, but also in those stable austenitic chromium-nickel steels which are prone to the formation of σ phase (in particular, 25-20-type steels). In view of the reduced rate at which diffusion occurs in austenite, ageing will, in the case of these steels, be a slower process, developing at higher temperatures.

Welding of Stainless-Steel Foil

J. CAMPBELL: 'Control of Process Variables: Key to the Successful Welding of Foil.'

Welding Jnl., 1959, vol. 38, Dec., pp. 1182–91.

The development of high-speed aircraft and missiles has involved complementary research on the development of structures which will combine the requisite properties of low weight and high strength. Subsequent to the design stage, it has frequently been found that the most suitable structures could not be fabricated, since the thin component sections could not be joined to produce mechanical properties in the joint equal to those of the parent metal. Welding, by the inert-gas-shielded tungsten-arc process appeared to offer the most promising method of satisfying this requirement, and an investigation was therefore initiated to determine the problems and variables involved in tungsten-arc welding stainless-steel foil. The findings of this work are reviewed in the paper.

The research was carried out on Type 302 18–8 chromium-nickel stainless-steel sheet 0·002, 0·003 and 0·005 in. (0·05, 0·075 and 0·125 mm.) thick. It is shown that inert-gas-shielded tungsten-arc welding is adaptable to the production of plain butt joints in stainless-steel foil, provided that the process variables are carefully controlled. Correct preparation of the joint edges and precise control of the welding-power input to the arc are prerequisite for optimum results. Edge preparation, the welding procedure, addition of filler metal to the weld pool, and the influence, on joint properties, of the current, arc length, travel speed and filler metal are discussed in the light of the results of the investigation, and the procedures used to produce butt joints in foil of each of the three thicknesses studied are outlined.

Tungsten-Arc Welding of Power-Pipe Joints

R. W. BENNETT: 'Tungsten-Arc Welding the Root Pass of Power-Pipe Joints.'

Welding Jnl., 1959, vol. 38, Dec., pp. 1175–81.

Designers, fabricators and erectors of power-pipe systems have, in joining pipe, long been confronted with the problem of producing weld joints which will be crack free, have complete root fusion and penetration, exhibit mechanical and physical properties equivalent to those of the basis metal, and provide an internal surface free from irregularities or constrictions. Developments in the welding of ferritic and austenitic steels by the inert-gas-shielded tungsten-arc process have stimulated the development of procedures capable of achieving optimum quality and uniformity in the root pass. In the U.S.A. the major proportion of the high-quality piping used in the power, chemical and petroleum industries is produced by the member companies of the Pipe Fabrication Institute. This report, prepared by the Metallurgical Committee of the Institute, 'contains the results of a literature survey, as well as information, correlated from the various companies of the P.F.I., on practices that have been found both suitable and economical for both shop fabrication and field erection of carbon, low-alloy chromium-molybdenum steels and the austenitic stainless steels'.

The sections of the report cover: weld-joint designs (involving discussion of the influence of the pipe size and material composition); end preparation; joint designs recommended by the Institute; fabricating conditions (tacking, purging the joint area, factors influencing control of the weld metal, welding technique); and general welding conditions recommended by the Institute for welding, without use of backing rings, the root pass in pipe joints.

ANALYSIS

Titrimetric Determination of Nickel in Non-Ferrous Alloys

See abstract on p. 70.

Determination of Nickel and Cobalt in Alloys and Stainless Steels

See abstract on p. 70.

Determination of Lead in Iron and Steel

See abstract on p. 84.

PATENTS

Production of Foam Materials from Nickel Powder

The foam material provided by the invention is, both at room temperature and elevated temperatures, strong, rigid, ductile, light in weight, and resistant

to oxidation, thermal shock and deformation; it maintains low-heat conductivity and the ability to control the flow of gases, vapours or liquids (as, for example, in its application as a seal material). The process involves the following steps: mixing nickel powder (99 per cent. pure and of 95 per cent. −325 mesh size) with a 100 per cent. solids methyl phenyl silane resin; heating the mixture to 400°F. (205°C.) for 1-2 hours to cause foaming; heating slowly (over a period of 2-5 hours) from 800°F. (425°C.) to 1200°F. (650°C.) in a hydrogen atmosphere; holding at 1200°F. for 1½ to 2 hours; increasing the temperature slowly to the range 1800°-2400°F. (980°-1315°C.); and holding at the latter temperature for 1-8 hours. A bridged cyanidine compound is preferably added to increase the rate of foaming.

The pore size may be varied by varying the volume of the mould and the amount of foaming agent added.

M. F. GRANDEY, assignor to GENERAL ELECTRIC COMPANY. *U.S. Pat.* 2,917,384.

Production of a Porous Nickel Surface on Vacuum-Tube Cathodes

A porous nickel surface is formed on the metal body of a vacuum-tube cathode by a process which comprises: coating the surface of the body with a film of organic binder (preferably nitro-cellulose); depositing a layer of nickel powder; heating (preferably in a controlled atmosphere in the range 960°-1000°C.) to sinter the layer of powder and volatilize the binder; coating the sintered layer with a further film of organic binder and depositing a second layer of nickel powder; and finally heating to sinter this second layer and volatilize the binder. The porous nickel surface so produced is stated to follow closely the original contour of the cathode surface and to require no machining or grinding.

MULLARD, LTD. (inventor, P. J. ELLIS). *Brit. Pat.* 827,150.

Influence of Nickel on the Production and Stability of Bacitracin

Bacitracin, which may be prepared by the cultivation of microorganisms, particularly *Bacillus subtilis*, has found considerable application in the preparation of feeds for poultry and livestock. Its incorporation into such feeds markedly stimulates growth, but the scope of the antibiotic is limited by its instability under ordinary storage conditions and by the fact that its production by fermentation methods involves considerable losses.

According to the present invention, addition of a water-soluble non-toxic nickel salt stabilizes the bacitracin against deterioration during storage. Moreover, incorporation of a water-soluble nickel salt into the aqueous fermentation mash, before evaporation and drying, minimizes the amount of bacitracin lost. In the former case, the concentration of the nickel is between 0·4 and 200 per cent. of the weight of the bacitracin; in the latter, the nickel concentration is between 0·1 and 5 per cent. of the weight of the mash.

R. A. ZORN, assignor to GRAIN PROCESSING CORPORATION. *U.S. Pat.* 2,903,357.

Prevention of Caking in Common Salt

Fluctuations in the value of the relative humidity have a major effect on the caking process in common salt (sodium chloride). At a value higher than about 70 per cent. salt crystals absorb moisture, which forms a saturated solution on their faces. When the relative humidity decreases, some evaporation of saturated solution occurs, resulting in the formation of crystal growths on, and attached to, the faces of the old crystals, which thus become bonded together. The firmer the bond, the greater is the degree of caking and the hardness of the cake.

According to the claims of the patent, the caking tendency of common salt is minimized by modifying the deposition characteristics of the reprecipitated material so as to preclude the formation of strong bonds between the original crystals. This modification is achieved by adding to the solid salt a substance which, in aqueous solution, gives rise to multivalent complex anions. Complex co-ordination compounds of cobalt and of iron, complex cyanides of chromium and ruthenium, cobaltinitrites, ferrioxalates, silicotungstates, and complex cyanides of nickel (e.g., potassium nickelocyanide) are claimed as additives.

IMPERIAL CHEMICAL INDUSTRIES, LTD. (inventors, C. ALLDAY and T. N. BELFORD). *Brit. Pat.* 818,385.

Method of Improving Smoking Qualities of Tobacco

High-quality cigarette and pipe tobacco is produced from poor-quality portions of tobacco leaves (which would normally be discarded) by treating the leaves with a solution of (1) up to 2 wt. per cent. of a primary catalyst consisting of at least one suitable salt selected from the salts of cobalt, manganese, copper, nickel, chromium, and silver, and (2) approximately 2 per cent. of a simple aliphatic acid from a group comprising acetic, phosphoric, tartaric, glycollic and lactic acids (an addition which renders the catalyst more effective). In the case of air-cured tobacco containing little or no sugar, the addition of about 10 per cent. of invert sugars, such as uncrystallizable syrups, molasses, honey, etc., has been found to enhance the effect of the catalysts.

The aim of the invention is to increase the degree to which the nitrogen bases present in the tobacco are thermally destroyed during smoking, and thus to reduce the alkalinity of the smoke.

D. TYRER and D. D. TYRER. *U.S. Pat.* 2,914,072.

Improvements in Electroless Nickel Plating

An article of catalytic material is chemically plated with nickel by a process which involves: circulating

an aqueous solution of a nickel salt and a hypophosphite through the plating chamber at 90°–100°C., immersing the article in the solution sufficiently long for deposition of the desired nickel coating (by reduction of the nickel cations to metallic nickel, with corresponding oxidation of the hypophosphite anions), and maintaining the solution at the predetermined composition by a regeneration treatment, outside the plating chamber, which includes the removal of phosphite and the addition of both a soluble nickel salt and a soluble hypophosphite.

GENERAL AMERICAN TRANSPORTATION CORPORATION. *Brit. Pat.* 822,407.

An aqueous chemical nickel-plating solution of the nickel-cation/hypophosphite-anion type characterized by (1) stability and a low plating rating (at a temperature well below its boiling point), and (2) instability and a high plating rate (at a temperature near its boiling point) is circulated, from a reservoir at a temperature ensuring stability, through a preheater and a condenser, into the plating chamber, which is at a temperature associated with a high plating rate, and then into a flash tank, an after-cooler, and finally back into the reservoir. The process claimed incorporates improved facilities for (*a*) continuously regenerating and then filtering the regenerated and circulated plating solution at a relatively low temperature, and (*b*) continuously heating the filtered solution to the plating temperature in a sequence of steps which minimizes risk of spontaneous thermal decomposition.

GENERAL AMERICAN TRANSPORTATION CORPORATION.

Brit. Pat. 822,408.
Similar to *Belgian Pat.* 545,050.
Similar to *French Pat.* 1,152,588.
Similar to *Australian Pat.* 213,436.
Similar to *Italian Pat.* 544,316.

Electroless Nickel Plating of Magnesium and Thorium

The object of the invention is the provision of an electroless nickel-plating solution exhibiting improved stability, even in the presence of magnesium and thorium (for the nickel plating of which it is particularly suitable).

The solution has an initial pH in the range 7–11 and contains:

	mole/L.
Nickel ion	0·005–0·2
Hypophosphite ion	0·01–0·4
Fluoride ion ..	0·2–1·0
Alkyl or alkanol amine	Sufficient to provide an N to Ni^{++} ratio of from 1 : 1 to 10 : 1.
Carboxylic acid or salt thereof (as a buffer)	Sufficient to produce a carboxyl-group / hypophosphite-ion ratio of from 1 : 1 to 10 : 1.

L. V. PULS and W. R. VINCENT, assignors to GENERAL MOTORS CORPORATION. *U.S. Pat.* 2,916,401.

Nickel Plating of Titanium and its Alloys

Titanium and titanium-base alloys are nickel plated by a procedure which involves (1) immersing them in a hydrofluoric-acid solution for a time sufficient to form a violet film, (2) rinsing them in water, and (3) electrodepositing nickel (at 5–40 amp./sq. ft.: 0·54–4·32 amp./dm.^{2}) from an aqueous electrolyte substantially free from metal salts of halogen acids and consisting of $NiSO_4.6H_2O$ 70–375 g./L. and sufficient sulphuric acid to adjust the pH to a value of about 0–2. In phase (3), the solution may consist of $CoSO_4.7H_2O$ and/or $NiSO_4.6H_2O$ 70–375 g./L. and sufficient sulphuric acid to ensure a pH in the range 0–6·2, in which case the current density is in the range 5–100 amp./sq. ft. (0·54–10·8 amp./dm.^{2}). The nickel, cobalt or nickel-cobalt coatings deposited remain firmly adherent at 1000°F. (540°C.).

D. HALPERT, assignor to VERTOL AIRCRAFT CORPORATION. *U.S. Pat.* 2,921,888.

Production of Protective Coatings on Uranium or Uranium-base Alloys

Uranium or uranium-base alloys are heated (preferably in the range 250°–600°C.) in contact with a mixture comprising a metal or metal-oxide powder (preferably aluminium, beryllium, nickel or chromium) and a powdered halide or oxyhalide salt (preferably of aluminium or an alkaline-earth metal). The metallic coating thus provided is adherent, electrically conductive, less readily oxidized than the uranium, and can serve as a basis for application of a further protective coating (e.g., by electrodeposition).

UNITED KINGDOM ATOMIC ENERGY AUTHORITY (inventors, R. A. U. HUDDLE and A. R. GIBSON). *Brit. Pat.* 829,089.

Gas-Deposited Nickel Coatings of Increased Electrical Resistance

The addition of ammonia gas to nickel-carbonyl plating gas has been found to result in the production of nickel-containing films of relatively high electrical resistance. Under the claims of the patent this finding is now applied to the preparation of electrical-resistance units.

The nickel-carbonyl plating gas, containing 4–8 vol. per cent. of ammonia (and preferably argon), is passed over electrical insulating material at a temperature sufficiently high (preferably 110°–140°C.) to decompose the nickel carbonyl; the plating time is sufficient to produce a nickel coating (preferably 0·1–1 mil thick) of high ohmic resistance.

O. J. CUMMINS, assignor to UNION CARBIDE CORPORATION. *U.S. Pat.* 2,921,871.

Nickel-Copper-base Alloys for Use in Glass-Moulding Elements

Alloys suitable for casting into moulds used in glass pressing fall within the following range of composition: copper 20–40, aluminium 0·5–17,

titanium 0·01–0·5, silicon 0·2–1·5, manganese 0·5–2·5, carbon 0·2 max., magnesium 0·02–0·1, boron 0·03–0·5, iron 0–2·5, cobalt 0–1, per cent., remainder nickel.

The alloys are preferably produced by a process which involves: treating a silicon-containing molten bath of nickel and copper with nickel oxide to remove oxidizable impurities; deoxidizing with silicon; adding the required amount of manganese; carburizing with not more than 0·2 per cent. of carbon; adding part of the aluminium content; adding the titanium; adding the remainder of the aluminium; adding boron; adding at least 0·05 per cent. of magnesium with or after the boron; and finally casting.

MOND NICKEL COMPANY, LTD. *Brit. Pat.* 829,684.

Nickel-Aluminium Bronzes

Aluminium bronzes falling within the following range of composition are used for moulded products of large dimensions (such as marine propellers, pump rotors and hydraulic turbines): manganese 8·5–9·5, aluminium 8·0–10·5, iron 2·5–5·0, nickel or cobalt 2·0–3·0, impurities < 0·25, per cent., remainder copper.

As a result of the iron and nickel alloying additions, the bronzes, which can be welded (even in sections of the order of 60 mm. thick) and are suitable also for use as forgings, are stated to combine the advantages of good resistance to sea-water corrosion or to cavitation erosion with excellent elongation characteristics, fatigue-resistance and resilience.

SOCIETE DES FORGES ET CHANTIERS DE LA MEDITERRANEE.
Brit. Pat. 828,759.
Similar to *French* „ 1,177,060.

Implements for Use in Inflammable or Explosive Environments

The working portions of implements (e.g., spades, shovels or pick axes) for use in an explosive or inflammable environment are coated with a deposit of non-sparking metal by brazing or welding. The basis metal may consist of steel or a non-sparking material (beryllium-copper is specifically claimed). The non-sparking coating is preferably an aluminium-bronze of the following composition: aluminium 8·5–10·5, nickel 3–5·5, iron 3–5·5, manganese 3 max., zinc 0·5 max., impurities 0·3 max., wt. per cent., remainder copper.

POWER-GAS CORPORATION, LTD., NORTH WESTERN GAS BOARD and S. MUNRO.
Brit. Pat. 818,271.

Production of Nickel-containing Magnetic Alloys in the Form of Thin Strip

Alloys which are inherently brittle at room temperature, and which therefore are not amenable to cold working, are converted into thin strip by compacting a mixture of the appropriate metal powders, sintering the compacted strip at a temperature which, while high enough to relieve internal stresses, is yet sufficiently low to maintain heterogeneity, cold rolling the sintered strip to the desired thickness, and finally homogenizing by further heat-treatment.

The preferred application is to the production of iron-nickel-aluminium(-cobalt) permanent-magnet alloys and of a binary cobalt-iron alloy.

MOND NICKEL COMPANY, LTD. (inventors, D. K. WORN and A. ECCLES). *Brit. Pat.* 829,640.

Heat-Treatment and Applications of an Aluminium-Cobalt-Copper-Nickel-Iron Permanent-Magnet Alloy

A permanent-magnet alloy of the composition indicated below is (according to the claims of *Patent* 1,074,611) cooled, over a period of about 5 minutes, from above 1200°C. to 500°C., cooled from 500°C. to room temperature, and finally annealed in the range 550°C.–650°C. to achieve a remanence of 7000–8000 gauss, a coercive force of 300–500 Oersted, a linear demagnetization plot, and high reversible permeability. The heat-treated alloy is used, in particular, for pre-magnetizing magnetically soft components, such as are incorporated in telephone ear pieces.

Patent 1,074,612 covers a heat-treatment (pertaining to the same alloy) which, except for the omission of the final annealing stage, is the same as that outlined above. In this case, the heat-treated alloy exhibits a remanence of at least 10,000 gauss and a coercive force in the range 80–200 Oersted. The alloy is used as a rotor material in hysteresis motors.

Limits of composition: aluminium 7–10, cobalt 20–30, copper 2–6, nickel 12–17, remainder iron.

BETEILIGUNGS- UND PATENTVERWALTUNGSGESELLSCHAFT m.b.H. (inventor, H. FAHLENBRACH).
German Pats. 1,074,611.
1,074,612.

Nickel-base Alloy for Neutronic-Reactor Applications

Although in the past the nickel-base alloys 'Inconel' and 'Hastelloy' have been commonly used in neutronic-reactor applications, neither material offers resistance both to simultaneous oxidation and fused-salt corrosion and to embrittlement during high-temperature reactor service. The alloys claimed in the patent are stated to combine the advantages of such resistance with those of ease of fabrication and of mechanical strength equivalent to that of previously available comparable materials. They contain: molybdenum 15–22, chromium 6–8, wt. per cent., a relatively minor amount of carbon, and, preferably, up to 4 wt. per cent. of at least one additional strengthening agent selected from tungsten, tantalum, vanadium and niobium, remainder nickel.

H. INOUYE, W. D. MANLY and T. K. ROCHE, assignors to UNITED STATES ATOMIC ENERGY COMMISSION.
U.S. Pat. 2,921,850.

Protection of Nickel-base Alloys against Attack by Fuel-Combustion Products

According to the claims of the patent, a metallic article, preferably a gas-turbine blade, is coated with a beryllium/aluminium or beryllium/magnesium layer which confers protection against attack by fuel-combustion products. The article, consisting preferably of an age-hardenable nickel-chromium- or nickel-chromium-cobalt-base alloy, is heated in contact with a mixture of metallic beryllium, either aluminium or magnesium (in metallic or compound form), and a solid halide which volatilizes under the heating conditions.

The following process is specifically claimed: the surface of an alloy containing chromium 20·1, titanium 2·24, aluminium 0·37, carbon 0·1, silicon 0·42, manganese 0·18, iron 0·31, per cent., remainder nickel, is enriched with beryllium and aluminium (or magnesium) by heating the alloy in contact with beryllium, ammonium iodide, and aluminium oxide (or magnesia) at 1020°C.

POWER JETS (RESEARCH AND DEVELOPMENT), LTD. (inventors, R. L. SAMUEL, N. STEPHENSON and T. A. TAYLOR).

Brit. Pat. 828,897.
Similar to *French Pat.* 1,189,107.
„ „ *Canad. Pat.* 578,313.

Creep-Resisting Austenitic Steel

The heat-resisting steels which form the subject of the patent are for use in applications requiring high creep-resistance at temperatures in the region of 700°C. Preferably, the final stage of hot working is carried out in the range 750°–900°C. to achieve a reduction in section of about 15 per cent.

Limits of composition: carbon 0·2 max., chromium 10–25, nickel 10–20, molybdenum 0·5–5 and/or tungsten 0·5–3, vanadium 0·3–1·5, copper 0·3–3, nitrogen 0·03–0·25, boron 0·01–0·5, per cent., niobium/tantalum at least 10 times the carbon content.

SCHOELLER-BLECKMANN STAHLWERKE A.G. (inventor S. MAYERHOFER). *Austrian Pat.* 6139/58.

Heat-Resisting Austenitic Alloys of High Strength and Low Notch-Sensitivity

Precipitation-hardenable austenitic alloys falling within the following limits of composition exhibit high rupture strength (at temperatures in the range 600°–700°C.) and low notch-sensitivity: nickel 20–35, chromium 7–23, manganese 0·3–2·5, silicon 0·1–1·5, tungsten and/or molybdenum 1·25–3·5, vanadium 0–0·5, aluminium 0–0·4, carbon ⟨0·1, titanium 1·6–3·5, boron 0·005–0·5, wt. per cent., remainder iron. The alloys may contain up to 20 per cent. of cobalt. The boron content increases with the titanium content, the boron having the effect of improving the properties of the alloy during precipitation hardening by causing optimal distribution of the hardening precipitate.

The improvement in notch-rupture life associated with such boron-containing alloys is exemplified.

WESTINGHOUSE ELECTRIC CORPORATION.
Brit. Pat. 826,712.

'Genuage' Ageing Treatment for Austenitic Heat-Resisting Alloys

The patent covers a multiple-stage ageing treatment, applicable to iron-base austenitic alloys rendered age-hardenable by 1·3–3·5 wt. per cent. of soluble titanium, which is stated to develop optimum creep-rupture properties in a relatively short total period of time.

The treatment, designated 'Genuage', comprises the following stages: (1) solution-treatment at a temperature higher than 1700°F. (925°C.); (2) rapidly cooling to below 1250°F. (675°C.); (3) re-heating to a first ageing temperature in the range 1100°–1250°F. (595°–675°C.) and soaking long enough (i.e., 2–50 hours) to cause nucleation of precipitation-hardening components (reflected in a rise in hardness of from 30 to 125 D.P.H. points); (4) heating slowly (over a period of 2–32 hours) to the range 1300°–1450°F. (705°–790°C.), and holding in this range until the hardness increases by at least 25 D.P.H. points. Alloys containing less than 1·4 per cent. of soluble titanium are preferably heated to 1100°–1200°F. (595°–650°C.) in stage (3), and to 1250°–1350°F. (675°–735°C.) in stage (4).

The application of the treatment to alloys falling within the following composition range is specifically claimed: nickel 10–35, chromium 7–23, tungsten and/or molybdenum 6 max., manganese 2·5 max., silicon 0·3–1·5, aluminium 0·5 max., vanadium 0·5 max., carbon ⟨0·15, boron 0·5 max., titanium 1·3–3·5, per cent., remainder iron.

T. W. EICHELBERGER, assignor to WESTINGHOUSE ELECTRIC CORPORATION. *Canad. Pat.* 590,807.

Descaling of Nickel-base Alloys after Heat-Treatment

The complex oxide films which form on nickel-base alloys during heat-treatment or hot working, and which are difficult, or impossible, to remove by previously available descaling techniques, are subjected, according to the claims of the patent, to a treatment which converts them to a scale susceptible to acid pickling. The alloy is immersed for not more than about 30 minutes in an aqueous bath containing acetic acid 5–30, hydrofluoric acid 0·5–17 wt. per cent., and from about 0·1 per cent. to saturation of titanium, the temperature of the bath being maintained between room temperature and 150°F. (65°C.). The scale is then removed by immersing the alloys in a second aqueous bath containing about 1–70 wt. per cent of nitric acid. The alloy is preferably coated with lime prior to heat-treatment.

The application of the descaling treatment to 'Inconel' is described.

D. R. ZAREMSKI and J. M. BEIGAY, assignors to ALLEGHENY LUDLUM STEEL CORPORATION.
U.S. Pat. 2,913,360.

Welding of Austenitic Stainless Steels

The method of fusion welding austenitic stainless steels covered by the patent involves deposition of weld metal stated to exhibit excellent high-temperature properties, ductility and impact strength after prolonged exposure to service temperatures in the region of 1350°F. (735°C.) without necessitating heat-treatment or working to develop such properties. The method is stated to be particularly applicable to the welding of Type 316 18-8Mo and Type 347 19-9Nb chromium-nickel stainless steels.

The following weld-deposit composition is claimed: carbon 0·1 max., silicon 0·3 max., manganese 1-6, chromium 14-17, nickel 7-10, molybdenum 1-2, niobium 0-0·5, wt. per cent., remainder iron. The chromium equivalent percentage, as defined by the sum $\%Cr+\%Mo+(1\cdot5\times\%\ Si)+(0\cdot5\times\%Nb)$, lies in the range 15-19·5, and the nickel equivalent percentage, as defined by the sum $\%\ Ni+(30\times\%\ C)+(0\cdot5\times\%\ Mn)$, lies in the range 10·25-13·5.

In the preamble to the patent the properties of the 18-8-2Mo weld deposit are compared with those of Type 347 stainless-steel weld metal.

BABCOCK AND WILCOX, LTD. *Brit. Pat.* 829,114.

Protection of Molybdenum by Nickel-containing Oxidation- and Abrasion-Resistant Coatings

Molybdenum or molybdenum-base-alloy components (e.g., turbine blades) intended for operation at elevated temperatures are protected against oxidation by application of a metallic oxidation-resistant coating. Where higher resistance to erosion, abrasion and impact are required, a second oxidation-resistant coating with the necessary characteristics is applied over the relevant areas of the first coating and is secured to the article by fusion of the first coating. A preferred process involves flame spraying the article with a powdered nickel-silicon-boron alloy, heat-treating at the fusion temperature of the alloy, applying an appropriately shaped nickel-chromium or nickel-chromium-iron-alloy foil 0·003-0·006 in. thick to surface areas requiring additional protection, heating in a reducing atmosphere to cause the foil to adhere by fusion of the first coating, and finally hardening the second coating by impregnation.

The application of the invention to turbine blades is specifically claimed and details of coating procedures employed for this purpose are given in the preamble to the patent.

GENERAL ELECTRIC COMPANY. *Brit. Pat.* 823,111.

Production of Ductile Heat-Resisting Coatings on Cermet Materials

Heat-resisting components (consisting of a dispersion of carbides, borides, nitrides or silicides of titanium, zirconium, chromium, molybdenum, tungsten, vanadium, niobium and tantalum or mixtures thereof, in a matrix of heat-resisting binder metal) are coated with a ductile adherent heat-resisting metallic layer claimed to confer increased resistance to oxidation and thermal and mechanical shock and to improve elevated-temperature properties generally. The basis material contains a low-melting phase, present as a result of interaction between the binder metal and its refractory-metal-compound constituents. The heat-resisting coating material is bonded to the basis material by heat-treatment, at elevated temperature, and the improvement comprises maintaining at least one of the materials at a solidus temperature approaching within 100C.° of its lowest melting point, in the presence of a liquid bonding phase, for a maximum of 120 minutes: this procedure inhibits excessive diffusion of embrittling agents into the coating material. The basis material is preferably pre-coated with a layer of a highly-diffusible bond-promoting alloy with a melting point lower than that of the basis or coating material.

The preferred refractory-metal compound is of titanium-carbide base, the preferred coating material is a ductile heat-resisting nickel-chromium alloy, and the preferred pre-coat layer consists of a nickel-base alloy.

Turbine blades coated in accordance with the invention are claimed, and various methods of producing the coatings are described.

SINTERCAST CORPORATION OF AMERICA.
Brit. Pat. 820,654.
Similar to *U.S. Pat.* 2,899,338.

Cladding of Metals by Casting Techniques

According to the present invention, the difficulties inherent in the cladding of metals by conventional hot-rolling methods are obviated by casting the cladding metal into an ingot mould, allowing the mould to stand long enough for a layer to solidify around the whole of the wall of the mould, and then pouring out the molten metal within this layer so as to leave the mould lined by the cladding metal. While the surface of this cladding is still plastic the core metal is cast into the mould to fill the cavity within the layer, and the resultant ingot is then shaped to fit an extrusion container and extruded to sheet or other desired shape.

Stainless steel, nickel-copper alloys, nickel-chromium or nickel-chromium-cobalt alloys, nickel and tool steel (any of which may be used with an iron or a mild-steel core) are given as examples of cladding materials, and reference is made also to the use of the technique to clad a nickel-chromium electrical-resistance alloy with nickel.

HENRY WIGGIN AND COMPANY, LTD.
(inventor, P. G. TURNER). *Brit. Pat.* 818,817.

Nickel-containing High-Temperature Brazing Alloys

The brazing alloys covered in the two patents are for use in joining materials such as high-alloy steels, stainless steels and nickel-chromium alloys. Those claimed under *U.S. Patent* 2,900,251 are of the following composition: nickel 30-60, tin 20-45, palladium 10-30, silicon 4-8, per cent. The limits

of composition of those covered in *U.S. Patent* 2,900,253 are as follows: nickel 58–68, tin 25–40, cobalt 3–10, per cent.

The alloys are stated to have oxidation-resistance equal to or better than that of the basis metal at temperatures higher than 1000°F. (540°C.), and to permit brazing to be carried out without serious impairment of the physical properties of the basis metal at or near the braze.

R. M. EVANS and H. E. PATTEE, assignors to THE TRANE COMPANY. *U.S. Pat.* 2,900,251.
„ „ 2,900,253.

Nickel-Chromium-Germanium Alloys for Brazing Stainless Steel

The alloys claimed are for use in brazing stainless-steel components intended for service at elevated temperatures. They are stated to have a high re-melt temperature and excellent flow characteristics, and to exhibit high oxidation-resistance at elevated temperatures. Composition limits are as follows (preferred contents are given in parenthesis): nickel 37–65 (57), chromium 5–40 (13), germanium 15–40 (30), wt. per cent.

J. A. McGURTY and E. S. FUNSTON, assignors to U.S. ATOMIC ENERGY COMMISSION. *U.S. Pat.* 2,901,347.

Copper-Nickel Alloy for Brazing Titanium or Zirconium

Titanium, zirconium or titanium–zirconium alloys are brazed, in the presence of an inert gas, at temperatures in the range 960°–1100°C., using a copper-nickel brazing alloy containing more than 50 per cent. of copper (and preferably consisting of copper 80, nickel 20, per cent.).

The brazing alloy is applied in the form of foil 0·0125–0·0625 mm. thick, and the brazing time must be sufficiently long to ensure diffusion of any brittle intermetallic compounds which might form.

IMPERIAL CHEMICAL INDUSTRIES, LTD. (inventor, E. A. TAYLOR). *French Pat.* 1,189,194.

Self-Fluxing Brazing Alloys

Self-fluxing brazing alloys which are 'air-proof' (i.e., permit the brazing operation to be carried out in air) contain copper 1–80 (10–30), nickel 5–50 (15–25), lithium 0·25–8 (1–2), boron 0·25–2·5 (0·7–1·2), per cent., remainder (14·5 per cent. min.) palladium.

The alloys are particularly suitable for brazing carbon and alloy steels.

N. BREDZS, assignor to LITHIUM CORPORATION OF AMERICA, INC. *U.S. Pat.* 2,903,353.

Brazing of Nickel and its Alloys

The patent covers a brazing technique suitable for joining a wide range of metallic articles, including those of copper, nickel, cobalt, iron, manganese or of an alloy based on one or more of these metals. The surfaces to be joined are coated with a brazing material consisting of a reducible oxygen-containing phosphorus compound, and are then brazed by being heated in contact with each other (at 700°–1150°C. and in a reducing atmosphere consisting wholly or partly of hydrogen).

MOND NICKEL COMPANY, LTD. *Brit. Pat.* 829,275.

Nickel-base High-Temperature Brazing Alloy

An improved nickel-base brazing alloy, suitable for use at temperatures up to about 1800°F. (980°C.), contains chromium 10–30, silicon 8–12, manganese 7–15, wt. per cent., remainder nickel.

The alloy is stated to have good flow characteristics and low erosion properties, and the joint, which can be brazed at below 2100°F. (1150°C.), exhibits good oxidation-resistance and strength up to 1800°F.

G. S. HOPPIN, assignor to GENERAL ELECTRIC COMPANY. *U.S. Pat.* 2,923,621.

Attention is drawn to the fact that many of the names of materials mentioned in The Nickel Bulletin are *Registered Trade Marks*.

A Publication prepared by the
DEVELOPMENT AND RESEARCH DEPARTMENT

PRINTED IN ENGLAND BY WIGHTMAN MOUNTAIN LTD.
WESTMINSTER, LONDON, S.W.1